A review of the combustion and emissions properties of advanced transportation biofuels and their impact on existing and future engines

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A B S T R A C T

The fundamental combustion and emissions properties of advanced biofuels are reviewed, and their impact on engine performance is discussed, in order to guide the selection of optimal conversion routes for obtaining desired fuel combustion properties. Advanced biofuels from second- and third-generation feedstocks can result in significantly reduced life-cycle greenhouse-gas emissions, compared to traditional fossil fuels or first-generation biofuels from food-based feedstocks. These advanced biofuels include alcohols, biodiesel, or synthetic hydrocarbons obtained either from hydrotreatment of oxygenated biofuels or from Fischer–Tropsch synthesis. The engine performance and exhaust pollutant emissions of advanced biofuels are linked to their fundamental combustion properties, which can be modeled using combustion chemical-kinetic mechanisms and surrogate fuel blends. In general, first-generation or advanced biofuels perform well in existing combustion engines, either as blend additives with petro-fuels or as pure "drop-in" replacements. Generally, oxygenated biofuels produce lower intrinsic nitric-oxide and soot emissions than hydrocarbon fuels in fundamental experiments, but engine-test results can be complicated by multiple factors. In order to reduce engine emissions and improve fuel efficiency, several novel technologies, including engines and fuel cells, are being developed. The future fuel requirements for a selection of such novel power-generation technologies, along with their potential performance improvements over existing technologies, are discussed. The trend in the biofuels and transportation industries appears to be moving towards drop-in fuels that require little changes in vehicle or fueling infrastructure, but this comes at a cost of reduced life-cycle efficiencies for the overall alternative-fuel production and utilization system. In the future, fuel-flexible, high-efficiency, and ultra-low-emissions heat-engine and fuel-cell technologies promise to enable consumers to switch to the lowest-cost and cleanest fuel available in their market at any given time. This would also enable society as a whole to maximize its global level of transportation activity, while maintaining urban air quality, within an energy- and carbon-constrained world.

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Contents

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1. Introduction

As stated by MacLean and Lave [1], the use of gasoline or diesel in an internal combustion engine is likely to remain the most cost-effective overall ground-based transportation propulsion system for the near future. However, concern over greenhouse-gas emissions and the potential for rapid increases in petroleum prices due to supply-demand constraints motivates a search for alternative transport fuels, as well as high-efficiency conversion technologies that can obtain the maximum motive power (energy) out of the available chemical fuels. Liquid fuels remain attractive for transportation because of their high energy density: a teaspoon of gasoline, diesel or jet fuel contains chemical energy equivalent to the kinetic energy of a 1000 kg vehicle being driven at 100 km/h [2].

The first developments in biofuels for transportation applications were based on the well-established processes of converting plant sugars into ethanol via fermentation, and the upgrading of vegetable oils via transesterification. Ethanol is a high-octane fuel compatible with the majority of spark-ignition, or gasoline-fueled, internal combustion (IC) engines on the road today, as long as it is blended with gasoline at a reasonable level [3]. The high-level of interest in ethanol as a biofuel was motivated by the seemingly easy merging with existing infrastructure and the relatively low cost of producing the fuel due to an existing and proven alcohol production industry.

Similarly, biodiesel gained importance for compression-ignition, or diesel, engines due to its relative ease of manufacture. The use of plant oils as a transportation fuel was suggested by the visionary Rudolf Diesel at the very dawn of our current internal-combustion-engine driven society, when he stated:

"the fact that fat oils from vegetable sources can be used may seem insignificant today, but such oils may perhaps become in course of time of the same importance as some natural mineral oils and tar products are now….they make certain that motor-power can still be produced from the heat of the sun, which is always available for agricultural purposes, even when all our natural stores of solid and liquid fuels are exhausted" [4].

Vegetable oils, in raw form, can be used as fuels for IC engines, but engine wear problems and poor combustion performance, as well as the related higher emissions levels, motivate extra fuel processing to convert the triglycerides in the raw oils to the fatty-acid esters known as biodiesel [3,5–7]. Traditionally, methanol has

been used during the trans-esterification reaction producing fatty-acid methyl esters (FAME), but ethanol or propanol have been suggested for improving the cold-flow performance of biodiesel fuels [6,7], and use of bioethanol can improve the sustainability of the resulting biodiesel [8,9], but this may come with associated cost increases.

Increasing concerns over the environmental impacts of so-called first-generation biofuels [10–14], which include ethanol from corn and biodiesel from soybean or other edible oils, has motivated efforts to find other feedstocks. The first efforts in this area focused on conversion of nonedible oils [15], from crops such as camelina [16,17] or jatropha [15,18–21], into biodiesel or synthetic hydrocarbons, while current efforts are focusing on finding ways of converting the cellulosic fraction of the biomass into a suitable fuel source [11–14,22–25]. Such cellulosic-derived fuels are commonly termed second-generation biofuels [12–14,26]. While ethanol is a possible fuel product from cellulosic biomass [13,14,22–25], there has been a significant increase over the past few years in the number of potential new fuel molecules, including methanol [27,28], butanol [14,25,29–31], longer-chain alcohols [32], furan-based molecules [33–35], and bio-derived synthetic hydrocarbons [13,23,35–39]. Third-generation biofuels are considered to be those fuels that are derived from algae feedstocks [40–46], which could be FAME [45,47] or synthetic hydrocarbons obtained from upgrading algal oils [26,47,48]. Production of synthetic hydrocarbon fuels, which store primary energy from solar or nuclear sources as chemical energy, directly from water and recycled carbon dioxide, after its capture from exhaust stacks or the atmosphere, has also been proposed [49–52]. These synthetic "solar fuels" [50–52] will have similar combustion properties to bio-derived synthetic hydrocarbons of the same molecular composition.

Within the aviation community, it has become clear that the conversion of the global aircraft fleet to operate on a new fuel molecule is unacceptable from a cost and logistical perspective. Therefore, all biofuels for aviation use must be "drop in", a term that means that the fuels must meet the general requirements of the ASTM specification for jet fuel (ASTM D1655) [53,54]. A standard has been created (ASTM 7566) that allows blends of up to 50% of synthetic hydrocarbon alternative jet fuels to be used when mixed with conventional commercial jet fuel, but, currently, only for select processes from specific feedstocks [55]. These synthetic hydrocarbon fuels can be obtained either through Fischer–Tropsch synthesis [36,38,39,53], or by hydrotreatment of

triglycerides from vegetable oils, or animal fats, to remove all oxygen content from the fuel [36,53,56,57].

The present review discusses the combustion properties of a range of advanced biofuels and the impact of these different properties on engine performance and exhaust pollutant emissions. The conversion technology employed, along with the biomass feedstock in some cases, determines the chemical content and molecular structure of the fuel molecules, which will affect the combustion chemistry and the resulting pollutant emissions when they are used in engines. It is important to clarify that this is only one of the many factors that will be important in the decision to choose a specific biofuel, and its associated conversion process and feedstock(s). The technical, economic and environmental issues surrounding the production of these advanced biofuels, including the availability, cost and sustainability of the feedstock [11,46,58–72], the efficiency and cost of the associated biological or thermochemical biomass-to-biofuel conversion technology [8,12–15,20,22–25,27–29,73–75], and the life-cycle greenhouse gas emissions [11,50,56,57,62,65,66,70,71,76–78], are complex topics that have been extensively discussed and reviewed elsewhere. In addition to biofuels, bioenergy can be harnessed by burning biomass in power stations to generate electricity which is then used in electric-drive cars [79], or even by directly burning biomass dusts within internal-combustion engines [80]; however, discussion of these topics is outside the scope of the present paper. Biomass can also be gasified into producer gas or synthesis gas (syngas), or be anaerobically digested to form biogas (biomethane). These are of current interest as potential fuels for stationary power generation, e.g. [81], but are not currently considered feasible transportation biofuels within the context of this review.

The basic types of advanced biofuels are discussed in Section 2, followed by the combustion properties of such fuels, grouped by the engine type that they are most compatible with, in Section 3. The review is intended as a high-level overview of the combustion and emissions properties of a broad range of advanced biofuels for non-combustion specialists. Many of the topics herein have been reviewed in detail in past publications and preference is given to these sources when available. The review will also discuss advanced-engine and fuel-cell technologies that can more-efficiently convert the chemical energy stored in the fuel into motive power (energy), i.e., increase fuel efficiency, while simultaneously producing lower exhaust emissions than traditional spark ignition (SI) or compression-ignition (CI) engines to meet future emissions regulations and improve urban air quality. The optimal properties of fuel blends for future vehicles will be determined through advanced-engine research, which already suggests changes from traditional gasoline and diesel specifications due to the move to low-temperature combustion. The potential operational improvements, in terms of efficiency and emissions, and fuel requirements of a selection of advanced engine and fuel-cell concepts are discussed in Section 4.

2. Advanced biofuel classification

Ethanol and fatty-acid methyl ester (FAME) biodiesel are well known first-generation biofuels, but the development of advanced conversion technologies that can make use of cellulosic feedstocks has identified an ever-increasing array of potential new fuel molecules. Biochemical enzymatic conversion technologies can convert cellulose to sugars that are then converted to ethanol [13,14,22,24], butanol [14,29,30], higher alcohols (pentanol, hexanol, etc.) [32,82–84], or other, more exotic, compounds, such as furans [33,35,85]. These cellulosic-derived second-generation biofuels are oxygenated hydrocarbon molecules with relatively small

numbers of carbon atoms, and their physical and chemical properties have an influence on their combustion efficiency and exhaust pollutant emissions [86,87]. Ethanol has been widely used as a fuel additive in gasoline and as a pure biofuel in Brazil [3,22]. Methanol can be produced via catalytic synthesis using gasified biomass or natural gas as a feedstock at high efficiencies [27,28]. Butanol has been suggested as a more-compatible fuel than ethanol for the gasoline fueling infrastructure and has received significant attention in the past few years [14,29–31]. Longer-hydrocarbon-chain alcohols [32,82–84] are even closer to hydrocarbons in their chemical structure and would also be compatible fuels. Furans are more exotic fuels that can be seen as potential fuel additives [34,35], or as intermediate products that can be upgraded to synthetic hydrocarbon fuels [35], similar to those that result from Fischer–Tropsch synthesis (see below).

Plant oils from second- and third-generation feedstocks, such as camelina [16,17,77], jatropha [15,18–21], and algae-derived oils [45–47,58,88,89], are made up of triglycerides with carbon chains of varying length. Whether non-edible oils from camelina and jatropha can be called second-generation biofuels, or should be lumped in with first-generation biofuels, is debatable [26], but the key concerns in selecting a biofuel are not its nomenclature, but rather its overall carbon footprint, its impact on engine performance and resulting life-cycle pollutant emissions, its compatibility with fueling infrastructure, and its overall cost compared to other options. Using existing transesterification processes with methanol, these triglycerides can be converted into three fatty-acid methyl ester (FAME) molecules, with glycerol as a byproduct [5]. FAME from camelina, jatropha or algal sources is a mix of methyl esters with carbon chains of lengths from 10 to 20 carbon atoms with the highest fractions in the C16–18 range [15,16,18–20,87,89]. Such plant-oil based FAME biodiesel fuels have been successfully used for some time in diesel engines, but have serious shortcomings with regard to cold start, fuel stability and cloud point [5,6,87,90]. One mechanism for overcoming these issues is to hydrotreat the triglycerides to remove all oxygen from the oil [73]. This process results in a hydrotreated renewable jet (HRJ) or renewable diesel fuel composed of straight- and branched-chain paraffin hydrocarbon molecules that are a major component of petroleum-derived jet and diesel fuels [37,48,53,56,57,73,77]. Hydrotreated or hydro-deoxygenated renewable jet and diesel fuels, sometimes also called hydro-processed esters and fatty acid (HEFA) jet or diesel fuels e.g., [56], can be considered to be synthetic hydrocarbons of a similar type to Fischer–Tropsch fuels.

Fischer–Tropsch (FT) synthesis, the most-common biomass-to-liquid technology, typically produces a mix of straight-chain alkane, or paraffin, molecules, which have a variety of hydrocarbon chain lengths [13,36–39,91–93]. Distillation/fractionation of this "bio-crude" will lead to fractions that are similar to gasoline, diesel and jet fuel [36,91–93]. Some fractions will be made up of longer chains with lower vapour pressure than would normally be used for heating oil or bunker fuel purposes and there will also be lighter fractions that are similar to natural gas, propane or butane [91]. It is possible to re-introduce the short-chain, high vapour pressure portion back into the reactor so that additional carbon groups will be added to produce higher-value fractions, and the long-chain hydrocarbons may be catalytically cracked into more useable fractions [36,92–94]. Fischer–Tropsch synthesis results in hydrocarbon molecules with no oxygen content, leading to excellent compatibility with existing engine and fueling infrastructure [37,94]. The lack of aromatic content in Fischer–Tropsch fuels can lead to issues associated with poor lubricity and seal-swell problems that must be overcome for it to be used within the current ground and air transportation fleets [36,94–96]. Aromatic compounds, such as benzene or toluene, are hydrocarbon molecules that are stabilized by shared electrons within their carbon-ring

structure, and are named as such due to their characteristic sweet smell. The Fischer–Tropsch products can undergo isomerization processing to create branched hydrocarbons for gasoline and jet-fuel applications, or reactions at high-temperatures can create aromatics and napthas [36,94], which could lead to a fully-renewable biojet fuel.

Fast pyrolysis liquid (PL), or bio-oil, is a biomass-derived fuel created by thermally cracking biomass and rapidly condensing the stream of product vapors and aerosols into a liquid [13,97]. Without additional refining, PL is high in water and solid content, acidic, not fully distillable and has a heating value about one half that of conventional liquid petroleum fuels on a volumetric basis [98]. It is typically a dark brown, single-phase liquid consisting of an aqueous fraction with low molecular weight, oxygenated compounds, and a tar fraction containing high-molecular-weight lignin constituents [99]. Although PL has been commercially produced for about 30 years within the chemical industry, it has only recently been considered as a viable biofuel. There are multiple problems associated with direct utilization of raw PL in engines [100,101], that indicate that only upgraded PL will make a viable transportation fuel. No commercially-viable upgraded PL has yet been produced, nor are any standards available for certification, but it is likely that upgraded PL will have similar properties to hydrotreated renewable jet or diesel fuels or the products of Fischer–Tropsch synthesis obtained from biomass-to-liquid technologies [102,103].

While many other possible conversion technologies can be proposed that could lead to a variety of possible hydrocarbons (some oxygenated), the resultant chemicals will typically be similar to the four fuel classes identified above: (i) alcohols or other short-hydrocarbon-chain oxygenates; (ii) FAME or other biofuels consisting of long-hydrocarbon-chain oxygenates; (iii) synthetic hydrocarbons, such as from FT synthesis or hydro-treated oxygenated biofuels (e.g., from vegetable oils, algae-derived oils, or PLs); or (iv) a mix of many compounds, some oxygenated, as in PL. The use of these different types of fuels in engine applications is discussed in the next section, which is organized by the types of fuels that could be used in the different engine technologies in primary use for transportation today.

3. Combustion and emissions properties of advanced transportation biofuels

An excellent overview of the combustion processes involved in different internal-combustion engine types, and the effect that first-generation biofuel properties have on these combustion processes and resulting emissions, is provided by Westbrook [87]. Our three most familiar transportation fuels are derived from different cuts within the distillation column of a petroleum refinery and are: (i) gasoline, with 4–10 carbon atoms per molecule; (ii) jet fuel, with 10–14 carbon atoms per molecule; and (iii) diesel, with around 15–22 carbon atoms per molecule [87]. The type of biofuels chosen for an engine technology can be inferred from this; short-chain alcohols are used as gasoline replacements, while long-chain esters (biodiesel) are used as diesel substitutes [87]. Westbrook points out that even first-generation ethanol and FAME biofuels are more similar to conventional petroleum fuels than they are different, but that the existing differences, even if small, need to be understood in order to determine the effects of different fuel blends on engine performance and identify optimal fuel blends [87].

A major driver for improved engine technologies has long been the increasingly-stringent exhaust-emission regulations imposed to improve urban air quality and human health. The key emissions of concern are: oxides of nitrogen (NO_x) [104–107], particulate matter (PM or soot) [108–110], unburned hydrocarbons (UHC) [105,111,112] or oxygenates such as aldehydes [3,22,86,113], and carbon monoxide (CO) [3,105,113,114]. Nitrogen dioxide readily forms from nitric oxide in the atmosphere and causes respiratory problems, can react with ammonia and moisture to create small particles that can cause or aggravate respiratory disease and heart disease, and can react with volatile organic compounds (VOCs), such as UHCs, to form ground-level ozone [104]. Ground-level ozone is a major cause of urban smog [111], and this ozone causes respiratory problems, especially in people with asthma [115]. NO_x emissions cause acid rain [116], which leads to (i) acidification of lakes and streams, lowering the pH and releasing toxic aluminum into the freshwater that harm fish populations [117], (ii) slower growth, injury, or death of plants and forests [118], and (iii) damage to buildings and statuary [116]. Sulfur oxide emissions (SO_x) also cause respiratory problems [119] and lead to acid rain and urban smog [120], and result primarily from sulfur present in the fuel; SO_x emissions have been greatly reduced with the introduction of ultra-low-sulfur diesel fuels since around 2007. Particulate matter (PM), or soot, emissions are especially harmful when they are below 10 μm in size, because they are transported deeper into the lungs, and are linked to respiratory and cardiac problems [108]. PM emissions also acidify lakes and streams, cause esthetic damage to stone and other materials, and are the main cause of reduced visibility, or haze, in the United States [108]. Oxygenated-UHC emissions, such as aldehydes and ketones, are toxic emissions that are currently unregulated [86]. Carbon monoxide reduces the oxygen-carrying capacity of the blood and can cause death at sufficiently high levels [114]. Carbon dioxide emissions typically depend upon the power produced, engine efficiency, and the hydrogen-to-carbon ratio of the fuel and, for normal engine operation, the net carbon footprint can be determined from that of the fuel feedstock and biomass-to-biofuel conversion process, instead of relying on engine tests. The effect of using advanced biofuels in different engine types on the vehicle's exhaust pollutant emissions will be discussed in the following sections.

3.1. Spark-ignition (gasoline) engine alternative fuels

3.1.1. Spark-ignition (SI) engine combustion process

A cartoon of the combustion process within a spark-ignition (SI, or gasoline) engine is provided in Fig. 1 [87,121]. In a traditional port-fuel-injection SI engine, the gasoline is injected within the intake manifold (port) upstream of the intake valve so that the fuel is pre-vaporized and well mixed with the air within the engine cylinder [122]. A spark ignites the mixture at the desired time within the piston's cycle of motion, and this spark-ignited flame kernel develops into a high-temperature turbulent premixed flame that propagates through the well-mixed fuel–air engine charge. The fuel–air ratio in SI engines is typically kept very close to the stoichiometric fuel–air mixture needed for complete combustion in order to use modern 3-way catalysts for exhaust treatment [123]. The pollutant emissions levels leaving the cylinder of a SI engine running at the stoichiometric fuel–air ratio can be very high due to high flame temperatures leading to high NO_x, and unburned fuel in the piston crevices leading to high unburned hydrocarbon (UHC) emissions; however, emissions from SI engines have been greatly reduced since the development of three-way catalysts, which can control the carbon monoxide, NO_x and UHC emissions [112,124,125]. These three-way catalysts require that the engine be operated near the stoichiometric fuel–air ratio required for complete combustion to avoid oxygen in the exhaust [2,124]. Unfortunately, N_2O, a strong and long-lived greenhouse gas, and UHC emissions can be high before the catalyst is warmed up following a cold start [2]. Indeed, up to 90% of the total UHC
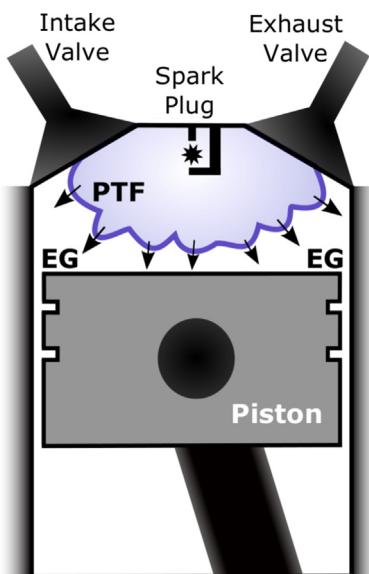
Fig. 1. Cartoon of the combustion process in a spark-ignition (gasoline) engine. A premixed turbulent flame (PTF) is formed after ignition from the spark, and propagates through a well-mixed fuel–air charge within the cylinder. The flame is colored blue as it is a non-sooting flame (cf. Fig. 2) and the flame emits chemiluminescence at several wavelengths that make the flame appear blue to our eyes. Engine knock occurs when the end gases (EG) auto-ignite after undergoing low-temperature cool-flame chemistry following their compression by the piston and by the advancing premixed turbulent flame.
Cartoon inspired by figures in Refs. [87,121].

emissions can be generated within the first 90 s after starting while the engine is cold [122]. For SI engines, the selection of a fuel depends on its auto-ignition properties, which are important for engine knock, the propagation speed of the premixed turbulent flame, and the resulting pollutant emissions.

Engine knock is an unfavorable engine operating condition, which can lead to significant engine damage, that occurs when pockets of unburned fuel–air mixture, termed end gases (EG), spontaneously ignite before they are consumed by the flame and result in rapid pressure rises in the cylinder [2,126,127]. The resulting pressure rise, or knock intensity, is directly proportional to the mass of end gases burned by auto-ignition [127]. Engine knock can be inhibited by using a higher octane, or less ignitable, fuel. The propensity for auto-ignition to occur is also dependent on the compression ratio of the vehicle's engine, since higher compression ratios lead to higher compressed-gas temperatures and faster end-gas reaction rates, such that engines with higher compression ratios demand higher octane fuel to avoid engine knock. Higher compression ratio engines lead to improved engine efficiency and, thus, better fuel economy; however, in a given engine with a fixed compression ratio, as long as the octane rating is above the required minimum, the octane rating of a fuel has no direct impact on engine performance.

The spark ignition leads quickly to a high-temperature turbulent premixed flame that propagates through the cylinder and consumes the well-mixed fuel–air charge. Therefore, the parameters that determine the influence of a fuel on its combustion efficiency, and resulting pollutant emissions, within SI engines are its flame temperature, the speed of the propagating combustion wave, or "turbulent flame speed", and the pollutant chemistry under these high-temperature flame conditions. The turbulent flame speed also determines the rate of pressure rise in the end gases which can affect end-gas auto-ignition and engine knock [2,127], with fast burning engine cycles more susceptible to knock as would be expected from the higher rate of end-gas compression [127]. Premixed turbulent flame propagation remains an active

area of combustion research, but it is generally understood that the turbulent flame speed scales with the laminar flame speed of the same fuel–air mixture and increases with increasing turbulence intensity [128,129].

3.1.2. Gasoline fuel combustion properties

Gasoline fuels [130], and other fuels used in SI engines, are specified by their octane ratings, which are a measure of the propensity of the fuel to auto-ignite. The different octane ratings of these fuels are due to differences in their low-temperature ignition chemistry [126,131–133], and fuels that ignite easily have low octane ratings, while those that are more difficult to ignite will have higher octane ratings [126]. The potential for the end gases to auto-ignite and cause engine knock is directly related to the propensity of the fuel to undergo an ignition process facilitated by the low-temperature chemistry characteristic of the "cool flame" combustion regime [134,135], because end gases undergo a two-stage ignition process where a cool flame proceeds hot ignition [135] and the associated rapid pressure increase. Cool flames are formed in the temperature range where the transition from low-temperature chemistry to high-temperature chemistry occurs [135]. High-temperature chemistry is involved in flame propagation and results in relatively complete conversion of the fuel carbon to carbon dioxide and fuel hydrogen to water (steam) [135], and will be discussed further below. Increasing the flame temperature will increase the rate of the high-temperature reactions due to the exponential dependence of Arrhenius reaction rates on temperature. Low-temperature chemistry depends on a complex competition between multiple chemical reactions involving alkylperoxy radicals [132,134–136]. The low-temperature chemistry results in a small temperature rise of the mixture due to competition from reactions whose rates inhibit the cool flame reactions at higher temperatures, resulting in the so-called negative-temperature coefficient region where the ignition delay times actually increase (meaning the mixture is less reactive) as temperature increases [132,135–137]. Cool flames emit a faint bluish light, resulting from the chemi-luminescent emissions of formaldehyde formed in excited electronic states [137], and typically occur in a temperature range from 500 to 850 K, although this varies with the system pressure [135,137]. Cool-flame low-temperature chemical reactions do not fully oxidize the fuel into carbon dioxide and water, but rather result in a mix of intermediate chemical species that include smaller hydrocarbon fuels, including methanol, aldehydes (formaldehyde, acetaldehyde), ketones, and peroxides [135]. If the end gases undergo a transition to a high-temperature second-stage auto-ignition, before they are consumed by the propagating turbulent flame, then engine knock results. Therefore, the propensity of a fuel to knock in an engine is directly related to the fuel's ability to undergo cool-flame reactions to enable auto-ignition at lower temperatures. Higher octane fuels, such as highly-branched alkanes, are less reactive at low temperatures than straight-chain hydrocarbons, which exhibit higher levels of low-temperature chemistry and thus have lower octane numbers [135]. Generally, the tendency for knock increases with hydrocarbon chain length in alkane fuels, and aromatic compounds have very low knock potential [134].

The octane scale is a relative measure of low-temperature auto-ignition process in a test engine with a fuel of interest, compared to a blend of the primary reference fuels (PRF): straight-chain *n*-heptane (research octane number, RON, of zero by definition) and highly-branched *iso*-octane (100 RON by definition) [126,131,138]. Gasoline fuels can contain up to 45% aromatic compounds, and it has been found that the aromatic hydrocarbon toluene (121 RON), must also be included in surrogate mixtures to capture RON dependence, specifically the non-linear and antagonistic effect of

blending toluene with *iso*-octane due to chemical interactions between the combustion intermediates of the different fuels in the blend [139,140]. Various blending rules have been proposed to predict the octane number of surrogate fuel blends [141], with some controversy over the optimum choice of blending rule [140,142].

Combustion chemistry models [143] for gasoline surrogate fuels, including primary and toluene reference fuels: *n*-heptane, *iso*-octane and toluene, have been developed [126,131,132,138,144,145] to model their fundamental combustion properties, which can be linked to their octane ratings [126,131,144]. These are generally quite large combustion models, with model size increasing with the chain length of the associated hydrocarbon fuel, including over 3000 reactions among over 700 species for individual gasoline surrogate molecules, slightly less for long-chain alcohols, and over 30,000 reactions among over 6000 species for the longest-chain biodiesel and petro-diesel surrogate molecules [136,146]. As one investigates longer hydrocarbon chains, all reactions associated with smaller hydrocarbons must be included, due to the hierarchical nature of combustion modeling [147,148]. Importantly, in high-temperature combustion of higher alkane and alkene fuels, reactions leading to C1 and C2 fragments are too fast to limit the overall rate of combustion and it is the oxidation rates of these smaller hydrocarbons that control most observed combustion properties [147,149,150]. Modeling results are not sensitive to the details of the various combustion chemistry models that have been proposed [136,146], since the intermediate species are inter-connected through complex reaction networks with very fast reaction rates between many common reaction partners. This inter-connectivity creates a local equilibrium that partitions the available carbon amongst these various possible intermediate species in a relative balance with each other [151]. The overall radical pool, therefore, evolves in unison, over space or time, as various species are added, by fuel breakdown reactions, or removed, by conversion of intermediates to stable combustion products, from the radical pool [146,151]. Therefore, even though the combustion chemical-kinetic mechanisms discussed above involve hundreds to thousands of different species, it is possible to reduce the mechanism size to around 50–100 species per surrogate fuel component while maintaining reasonable simulation accuracy of major combustion properties [136,138,145,152–155]. The number of additional intermediate species that must be added to the model, to maintain consistent accuracy, per surrogate-fuel component decreases as the total number of surrogate-fuel components increases [156,157], because many of the intermediate chemical species are shared between all hydrocarbon fuels [146–152]. Simplified 2-step models that use empirical fitting to match high- and low-temperature chemical behavior have also been proposed, e.g. [158].

3.1.3. Alcohol fuel effects on SI engine performance and emissions

Ethanol has been widely used as an octane-enhancing gasoline additive for SI engines as it has a RON of 109 [140]. Ethanol synergistically increases the octane rating of a blend with *iso*-octane non-linearly such that the octane number of a blend with 20–80% ethanol can exceed that of neat ethanol, but antagonistically decreases the octane rating of a blend with toluene non-linearly, such that the overall effect of ethanol on a specific gasoline fuel depends on the relative composition of branched alkanes and aromatics in the fuel [140]. In Brazil, it has been used neat in engines for some time, with slight vehicle retrofits required to replace some incompatible components [3]. Oxygenated biofuels are typically polar solvents and, thus, can be corrosive to engine and fuel handling materials, especially rubber or plastic tubing, pump housings, and some metallic parts [3,87]. The main issue with use of ethanol as a transport fuel comes from its lower energy density; it contains only around two-thirds of the energy of

a similar volume of gasoline [159] or other hydrocarbon fuel. This is not an issue during normal driving of an ethanol-fueled vehicle, as the driver will automatically adjust the accelerator position to control the power output of the engine to achieve the desired driving state; however, it will result in reduced vehicle range and a lower peak power of the engine when the accelerator is fully depressed. The higher octane rating of ethanol as compared to gasoline can allow higher compression ratio engines to be used, which can then lead to higher fuel efficiencies. Fuel-grade ethanol can be blended up to 10% by volume with gasoline for use as an automotive spark-ignition engine fuel in the U.S. [160], or up to 85% by volume (E85) for flexible-fuel engines [161].

Methanol, known as wood alcohol due to the historical process for obtaining it via the destructive pyrolysis of cellulosic feedstocks, is the shortest-chain alcohol. Methanol has the lowest energy content per liter of all liquid pure-component biofuels, approximately one half that of gasoline, and an octane rating of 112 [159]. The advantage of methanol is that it has the highest hydrogen-to-carbon ratio of all alcohols, and thus the minimum carbon dioxide emissions per unit of energy. It has also been proposed that methanol can be produced at much higher energy efficiencies than ethanol or other fuel options [28], especially if both biomass and natural gas are used as co-feedstocks [27]. In engines, soot emissions and benzene emissions, as well as other aromatic compound emissions, are much lower, but methanol is toxic and its flames have lower associated blue-chemiluminescence emissions, making the flames harder to see and increasing potential safety hazards [3]. Methanol also requires special fuel-system materials to prevent corrosion [87], but fuel-grade methanol can be used in blends with gasoline up to 85% (M85) for M85 flex-fuel engines within the U.S. [162]. Methanol is also a possible fuel for the direct methanol fuel cell [163,164], and is also an excellent candidate for on-board reforming to syngas or producer gas [22,27,164], which is a mix of hydrogen and carbon monoxide in diluents, due to methanol's high hydrogen-to-carbon ratio. The hydrogen-rich gas that results from this on-board reforming can be converted directly to electrical power in a high-temperature PEM fuel cell [165] or a solid oxide fuel cell [163,164,166], as further discussed below in Section 4.4.

Another possible biofuel proposed for spark-ignition engine applications is butanol, whose isomers have research octane numbers ranging from 96 for straight-chain *n*-butanol [85] to 105 for the highly-branched *tert*-butanol (which in a pure form is a waxy solid at room temperature) [167]. Butanol has a higher energy density than ethanol that is closer to gasoline, at about 90% of the volumetric energy content of typical hydrocarbons [14,29,167]. Butanol is not water soluble, while both methanol and ethanol are, and thus is a more attractive fuel for mixing with gasoline because it can be transported in existing pipelines and is more compatible with the existing fueling infrastructure [14,29]. Butanol isomers can be blended up to 12.5% by volume with gasoline for use as an automotive spark-ignition engine fuel in the U.S., except for *tert*-butanol due to its different physical properties from the other isomers [168]. Longer-chain alcohols, such as pentanol [32,82,83] and hexanol [32,83,84], have properties even more similar to hydrocarbon fuels and, thus, improved compatibility with existing engines.

The higher octane rating of ethanol results from reduced alkyl-peroxy and hydro-peroxy-alkyl, or cool-flame, reactions possible with the oxygenated molecule, compared to a hydrocarbon fuel, under the low-temperature combustion regime that controls auto-ignition in a SI engine [169,170]. When blended with hydrocarbon fuels, ethanol acts as a sink of reactive species (OH radicals) that disrupts the chain branching of the hydrocarbon fuel under low-temperature chemistry conditions and slows ignition of the blend [140,169]. Butanol, similarly, is seen to retard the low-temperature

chemistry of *n*-heptane, a gasoline primary reference fuel and common surrogate fuel-blend component, by fundamentally changing the reaction pathways of the hydrocarbon fuel when it is added to a blend, thereby increasing the octane rating of the fuel blend [171,172]. As the hydrocarbon chain increases from *n*-butanol to *n*-hexanol, the reactivity at low temperatures increases, due to more low-temperature chemistry for the long-chain alcohols [173]. *n*-Pentanol is the shortest-chain alcohol to exhibit significant low-temperature chemistry [174], and the inhibiting effect of the alcohol's hydroxyl functional group on low-temperature reactions decreases as the hydrocarbon-chain length increases for even longer hydrocarbon chain alcohols [175]. Studies of non-premixed low-temperature ignition quality tests, which are important for diesel engines as discussed in the next section but are also relevant to auto-ignition and engine knock, show a similar influence for ethanol and the different butanol isomers on the ignition propensity of the hydrocarbon base fuel [176], suggesting similarities in the low-temperature ignition chemistry of these alcohols.

It is, however, the high-temperature flame chemistry that controls the combustion efficiency and pollutant emissions in SI engines. After ignition by the spark, a turbulent premixed flame propagates through the premixed fuel–air charge in the engine, rapidly converting the fuel and oxygen into combustion products and the thermal energy and pressure that drive the engine (see Fig. 1). Straight-chain and cyclic hydrocarbons (alkanes, cyclo-alkanes, etc.) have higher laminar flame propagation speeds than branched-chain hydrocarbons or aromatics [145,177,178], with propagation speed decreasing with the level of hydrocarbon fuel branching [178]. For example, in a gasoline surrogate fuel study, it was shown that the flame speed increased in the order: *iso*-octane < toluene < gasoline < *n*-heptane, and that a mixture of 1/3 *n*-heptane, 1/3 *iso*-octane, and 1/3 toluene, by volume, matches the observed flame speed of a select gasoline fuel [177]. The flame speeds of different alkyl aromatics is also very similar [179]. Ethanol and butanol have been shown to have similar laminar flame speeds in air under fuel-lean to slightly-fuel-rich conditions [180–182]. These alcohols also have somewhat higher flame speeds than *iso*-octane [181–185], and *n*-heptane [183], which implies that flames will propagate faster in gasoline–alcohol blends than for pure gasoline. The flame speed decreases as the amount of fuel branching increases in the butanol [182,186] and pentanol [187] isomers, consistent with the effects seen in alkane fuels discussed above. The high-temperature ignition behavior, which results from chemistry similar to that occurring within flames, of the normal alcohols from ethanol to butanol is very similar for lean to stoichiometric mixtures, at fixed dilution ratios and reaction stoichiometries, over a range of pressures [188]. The high-temperature ignition properties of *n*-butanol to *n*-octanol are also seen to collapse [173,175], implying that high-temperature reactivity of all normal alcohols longer than methanol are similar. Under high-temperature conditions, alcohols from *n*-butanol to *n*-hexanol are more reactive than alkanes from butane to heptane (which collapse as well) [172,173], and increased fuel branching decreases reactivity [167,189,190], consistent with the observations on flame speed discussed above. The differences in high-temperature reactivity appear to be diminished as the length of the hydrocarbon chain in the alcohol increases [175]. The observed similarities in the high-temperature combustion behavior of alcohol fuels of different chain lengths are important, as they indicate that the flame properties will be similar in different engine technologies and, thus, these fuels are interchangeable from a combustion standpoint. The only exception is methanol, which exhibits significantly faster flame propagation under stoichiometric to fuel-rich conditions [148,180]. While the faster turbulent premixed flame speed could result in higher compressed end-gas temperatures, the reduced low-temperature chemistry from methanol will prevent auto-ignition and engine knock; therefore, the faster flame speed would have a positive impact on engine performance because it leads to faster, more-complete combustion. Indeed, a recent flame-visualization study within an optically-accessible engine has confirmed that the methanol blend (M85) produced the highest in-cylinder flame speed, with the ethanol blend (E85) slightly faster than either gasoline or *iso*-octane, which were similar to each other [191]. Another recent study observing flames in optically-accessible engines showed that ethanol flames propagate faster than butanol, followed by gasoline and *iso*-octane [192], consistent with the laminar flame experiments discussed above [180–185]. Recent experiments have shown that turbulent premixed flames of alkane fuels with 4–8 carbon atoms collapse for stoichiometric to fuel-rich mixtures, but fuel-dependent local extinction occurs for the lean mixtures due to the lower diffusivity of the long-chain fuel molecules compared to the oxygen or thermal diffusivities [193], which has implications for gasoline engines.

Detailed combustion models have been developed for methanol [148], ethanol [86,148,194], propanol isomers [86,148], butanol isomers [86,148,167,186,195–197], some pentanol isomers [174,198], *n*-hexanol [199,200] and *n*-octanol [175]. A detailed review of alcohol combustion properties, and the associated chemical kinetic modeling efforts to date, is provided by Sarathy et al. [201]. These models allow the combustion properties of these fuels to be simulated over a comprehensive range of thermodynamic conditions; however, there remains a need for more high-pressure data for model validation [148], especially of pollutant emission properties at high pressures [201].

Generally, PM (soot) emissions from port–fuel–injection SI (gasoline) engines are relatively low compared to CI (diesel) engines [122,125], and use of oxygenated biofuels generally reduces these PM emissions [3], since the carbon–oxygen bonds in the oxygenates reduce the number of carbon atoms that are active in the radical pool responsible for soot formation [146]. The effect of alcohol fuels on soot formation is discussed further in the context of CI engines in Section 3.2.5 below. New direct-injection engine technologies result in higher PM emissions that are a concern, as discussed in Section 3.1.5.

Engine studies have shown that increased ethanol in the fuel can lead to increased oxides of nitrogen, or NO_x, emissions [3], while other studies have shown decreases for ethanol–gasoline blends (see discussion by Lynd [22]). Recent papers still do not produce consistent trends in relative NO_x potential of gasoline–alcohol blends [202–205]. NO_x is produced from a number of mechanisms in combustion devices, the two most important for the present discussion are: the thermal or Zel'dovich route, initiated when oxygen and nitrogen are available at high temperatures (> 1800 K), and the prompt route, initiated by CH radicals formed from the fuel species [105,106,206,207]. Alcohol fuels have slightly lower adiabatic flame temperatures at the stoichiometric fuel–air ratio than the corresponding alkane fuels and, thus, have slightly lower associated NO_x emissions through the thermal mechanism [208], but the thermal effect is relatively small for these fuels compared to the effect of the fuel chemical structure on prompt NO formation. Methanol has been shown to produce lower NO_x emissions for stoichiometric to fuel-rich flames than its hydrocarbon analog, methane, primarily due to the reduced production of prompt NO during methanol combustion [208,209]. The reduction in prompt-NO formation is due to the lower levels of CH-radical precursor species in methanol flames compared to those of hydrocarbons [146,208,209]. It is chemi-luminescence from excited-electronic-state CH radical species that gives flames their blue color, and the low light-emission intensity of methanol flames discussed previously is a direct visual indicator

of their lower CH, and hence lower prompt-NO, production. NO measurements and model predictions in ethanol flames are approximately half those in hydrocarbon flames [146,210]. Fundamental experiments looking at relative NO_x formation between butanol isomers and their non-oxygenated hydrocarbon analog, butane, in laminar flames show that the butanol fuels produce lower NO_x concentrations for all fuel–air mixtures, with the largest differences for rich mixtures [211]. This is again likely caused by the presence of the hydroxyl functional group in the alcohol acting to reduce the levels of CH produced in these flames, relative to hydrocarbon fuels, and thereby lowering NO formation through the prompt route [146]. Indeed, in a recent study, it was shown that the C1–C3 alcohols all produce lower NO emissions and CH radicals than their corresponding alkanes, and that the level of prompt-NO and CH radicals increase for increasing hydrocarbon chain length for both the alkanes and alcohols [208]. Higher levels of fuel branching lead to lower CH levels, but the level of prompt NO formed is also dependent on the flame speed of the mixture because this controls the residence time of the mixture within the prompt-formation region of the flame [212]. The effect of the alcohols gets smaller as the hydrocarbon chain length increases, with smaller differences between butanol and butane isomers than seen for the smaller alcohols/alkanes [212]. Since it has also been observed that the production of CH and NO increases with increasing hydrocarbon-chain length for small hydrocarbons [146,208,213,214], with the level of CH appearing to level off for the longest chains studied so far [214], it can be inferred that alcohol fuels, especially the short-chain alcohols, produce fundamentally lower NO_x emissions than commercial gasoline or diesel hydrocarbon fuels under similar fuel–air stoichiometric ratios. The concentration of CH radicals increases with the carbon content of the fuel–air mixture [151], indicating that mixtures of the same stoichiometry, and similar H/C ratios in the fuel, should show similar CH levels. Recent experiments have shown that the predictions of CH and NO profiles for alkane and alcohol fuels, from methane and methanol to butane and butanol, in well-characterized laminar stagnation flames varies greatly from model to model [207,208,212,214], with relatively high uncertainties evident in all NO_x formation routes [215,207]. More validation experiments, especially at high-pressure conditions relevant to modern engine technologies, are needed to improve these models for use as design tools. In summary, alcohol fuels have fundamentally lower NO_x emissions at the same stoichiometric fuel–air ratios than their petro-fuel analogs, but the difference gets smaller as the hydrocarbon chain within the alcohol gets longer [212]. The results of specific engine tests can be affected by engine-specific complications that lead to higher NO_x, but such engines could likely be tuned to produce lower NO_x during alcohol fueling compared to gasoline fueling.

Of significant concern when gasoline is replaced with an oxygenated biofuel is a potential increase in oxygenated emissions, such as formaldehyde, acetaldehyde and ketones [3,22,86,210]. SI engine tests have shown a trend of increasing formaldehyde and acetaldehyde emissions with increased ethanol blending [113]. These aldehydes are toxic, carcinogenic compounds whose emission levels are, as yet, unregulated. Such aldehydes also play a role in the formation of photochemical smog [111]. While some knowledge of the combustion chemical pathways of these fuels, and the resulting influence on pollutant formation, is available e.g., [86,201], more work is needed to identify how changes in the fuel molecular structure influence the formation of these oxygenated hydrocarbon pollutants.

3.1.4. Other alternative fuels and fuel additives for SI engines

Other potential alternative fuels of interest as gasoline additives are furan- or furfural-type molecules [33–35,85]. These fuel molecules can be obtained from sugars [33], or directly from cellulose [34], and can either be used as a fuel themselves, or can be upgraded into synthetic hydrocarbons using upgrading techniques [35]. Measurements of the fundamental flame propagation and ignition delay times of some furan-based biofuels have been published in the combustion literature [216–221], and combustion chemistry models have been proposed [85,218,222]. More studies on their combustion properties are needed if these are to become significant fuels or fuel additives.

FT or hydrotreated-renewable fuels are typically not as suitable for spark-ignition engines due to their lower attendant octane ratings. Such fuels can be used if they undergo processing to branch and isomerize the fuels [94,223], or through blending with ethanol or other ignition retarding additives, such as methyl *tert*-butyl ether (MTBE) [85,126]. Use of MTBE is known to cause groundwater contamination due to its high water solubility and has been associated with negative health impacts [159], although the toxicity risk of MTBE is not entirely clear [224–228]. Ethanol or butanol make good octane-improving additives to replace MTBE due to the fact that ethanol, while water soluble, is relatively non-toxic and butanol has low water solubility.

3.1.5. Direct-injection spark-ignition (DISI) engines

Spark-ignition (SI) engines have lower efficiencies than the other internal-combustion engines discussed in this paper because of "breathing" losses due to the pressure drop across the throttling valve that controls the intake air flow into the engine and its resulting power output, the lower compression ratios allowed by the octane ratings of the existing gasoline fuels, and high heat losses to the cylinder walls due to the high flame temperatures [2,122,124,229,230]. One strategy to improve the fuel efficiency of gasoline engines has been to eliminate the throttle and control the engine power by varying the total amount of fuel injected directly into the engine cylinder per cycle, termed gasoline direct injection (GDI) or direct-injection spark-ignition (DISI) engines [122,124,231]. These direct-injection systems can provide moderately-improved fuel flexibility, allow higher compression ratios, due to charge cooling as the fuel is vaporized within the cylinder lowering knock potential, and eliminate the throttle losses and reduce heat losses to the cylinder walls, thereby achieving a 20–25% higher fuel economy than traditional port–fuel–injection systems [122,124].

Such GDI/DISI direct-injection strategies require using higher-pressure fueling systems, which can enable the finer atomization of the fuel droplets needed to allow the fuel to mix and vaporize with air before being consumed by the flame [122]. The resulting fuel–air mixture is stratified with higher fuel-concentrations near the spark igniter to enable successful ignition and reduced fuel–air ratios towards the piston and cylinder walls [122,124]. The effect of stratified mixtures on turbulent flames is a topic of ongoing study in the combustion community, e.g. [232]. If the fuel droplets sprayed by the direct-injection system are large, then they burn in a non-premixed mode that leads to high soot and NO_x emissions [122,125], and liquid fuel impingement on the piston or cylinder surfaces will lead to UHC and soot emissions [112,124]. Generally, the reduced mixing in DISI engines compared to port–fuel–injection SI engines results in higher soot and UHC emissions, increased NO_x emissions, and the use of fuel-lean mixtures prevents the use of traditional 3-way catalysts due to the oxygen in the exhaust [122,125,231]. While the elimination of a fuel soak on the upstream (port) side of the intake valve results in reduced cold-start UHC emissions and the higher engine efficiency reduces CO_2 emissions per passenger mile [122], DISI engines may not be able to meet increasingly-strict PM emissions limits without resorting to using a gasoline particulate filter as an after-treatment remedy [125]. In order to allow DISI operation with reasonable emissions

and high efficiency, the engine operation mode is typically varied from a late-injection stratified engine charge diluted with exhaust gases at low loads and speeds, similar to a spark-assisted compression-ignition engine (see next section) or a low-temperature combustion compression-ignition engine (see Section 4.2), to an early-injection well-mixed engine charge that is shifted towards the stoichiometric fuel–air ratio at the highest speeds and loads, which is effectively a homogeneous-charge compression-ignition engine (HCCI engine, see Section 4.1) [122,124]. As will be discussed later, future engine designs will increasingly employ low-temperature combustion to improve efficiency and emissions which will blur the line between spark-ignition (SI) and compression-ignition (CI) engines.

3.2. Compression-ignition (diesel) engine alternative fuels

3.2.1. Compression-ignition (CI) engine combustion process

A cartoon of the compression-ignition (CI, or diesel) combustion process is given in Fig. 2 [87,121,229,233]. In a CI engine, diesel fuel is injected after the air is compressed to high temperatures and pressures, so there is no risk of engine knock from auto-ignition. This allows CI engines to employ higher compression ratios which lead to higher efficiency than SI (gasoline) engines. They also do not employ throttling valves as do SI engines, and thereby avoid the associated "breathing" losses, resulting in a typical efficiency premium of 20–40% over SI engines [2]. Our understanding of the combustion process in CI engines has been greatly improved through the pioneering in-cylinder imaging experiments, and the resulting model, by Dec and co-workers [229,233]. Fuel droplets are sprayed into the cylinder from multiple fuel injectors. The fuel droplets must vaporize and mix effectively with the air before burning in order to reduce soot emissions, but must also burn fast enough to avoid unburned hydrocarbon emissions. CI engines typically produce high levels of soot (PM) emissions due to the fuel-rich combustion zones that

Fig. 2. Cartoon of a CI (diesel) engine combustion process. Fuel droplets are sprayed into the cylinder from multiple fuel injector nozzles. The droplets vaporize and mix with air and are then partially combusted in a rich partially-premixed flame. The combustion intermediates from the partially-premixed flame are then burned with air in a non-premixed flame (NPF). The non-premixed flame is orange because soot, which is formed on the fuel side of the non-premixed flame, incandesces and gives the flame the orange-yellow color familiar from candle flames and wood fires.
Cartoon inspired by figures in Refs. [87,121,229,233].

result from the non-premixed and partially-premixed flames that occur in diesel spray combustion [110]. As pointed out by Weinberg [234], combustion in non-premixed flames results in the worst possible situation: flames that adjust to the maximum possible temperature, leading to high NO_x emissions, and that produce high concentrations of fuel at high temperature on the fuel side of the flame, leading to high soot emissions. If this soot is not burned out by mixing with high-temperature air, it can escape into the exhaust where it is released into the atmosphere unless filtered out by exhaust after-treatment systems.

3.2.2. Diesel fuel combustion properties

Diesel fuels [235], which traditionally fuel CI engines, are made up of longer-chain hydrocarbons that come off at a higher temperature in the distillation column of a traditional refinery than either gasoline or jet fuels [236]. The cetane number is a diesel-fuel property that measures the ignition propensity of a fuel sprayed into a standard engine-test apparatus. Higher cetane values indicate that a fuel will ignite more readily, so that a high-cetane fuel will, by definition, have a low octane rating; however, it should be noted that engine knock (octane rating) occurs within fully-vaporized and premixed fuel–air mixtures at slightly fuel-lean to stoichiometric conditions, while the cetane number depends on fuel-rich ignition after the fuel droplets have vaporized and partially mixed with air in the CI engine [87,131]. The ASTM D975 standard requires a minimum cetane number of 40 for regular diesel fuel [235], with values of 40–55 typical [85]. The cetane number is influenced by the fuel spray characteristics and the fuel volatility, and also by the low-temperature combustion chemistry. Generally, larger hydrocarbon chains have lower volatility, while increased chain branching yields higher volatility for the same number of carbon atoms [170]. Under high-pressure diesel injection in modern engines, vaporization is limited by the mixing and entrainment processes in the diesel fuel spray, rather than on droplet or atomization processes [237].

Low-temperature ignition chemistry is, therefore, the major determinant of a fuel's cetane number. Surrogate fuel compositions and combustion chemical-kinetic models, containing thousands of species and tens of thousands of reactions per surrogate component [146], have been developed for the complex mixture of long-chain hydrocarbons that make up diesel fuel [131,132,236,238,239]. Typical surrogate components used to model diesel fuel will be long-hydrocarbon-chain alkanes, both straight-chain and branched-chain isomers, such as the straight-chain *n*-cetane (cetane number of 100) and the highly-branched *iso*-cetane (cetane number of 15) [240], as well as aromatic compounds, including toluene (mono-aromatic) and tetralin (naphtha-aromatic) [145,236]. The cetane number is seen to be strongly correlated with the computed ignition delay time using fundamental models [87], with reduced reactivity and longer ignition delay times for highly-branched hydrocarbons leading to lower cetane numbers [87,240], and little sensitivity of the low-temperature chemistry is observed for variations in the hydrocarbon chain length of long-chain fuels [239]. While cetane number correlates with low-temperature ignition properties of different fuel molecules, a complete model has yet to be developed to fully link the cetane number found from experiments in ignition-quality testers for diesel fuels to the fundamental physical and chemical properties of the fuel blend [176]. The conceptual model by Dec [233] has been used by Westbrook and co-workers to explain a number of phenomena in CI engines caused by variations in cetane number and the associated fuel chemistry [87,126,131,238–241]. More research is needed to inform modeling of the formation of pollutant emissions within the complex flame structure that exists within the CI engine [110,126,131,237], as well as how to optimize the cetane number for a specific engine application or how to tune an existing engine for a new fuel blend.

3.2.3. Biodiesel effects on CI engine performance and emissions

FAME biodiesels derived from food-based feedstocks were one of the earliest biofuels of significant interest and, therefore, have received extensive study [3,5–7,86,87,238,242–253]. FAME can be blended up to 20% with petroleum diesel based on the ASTM D-7467 and ASTM D-6751 specifications [254,255]. In Europe, up to 7% FAME can be blended in ultra-low-sulfur diesel fuel, per the EN 590 standard [256], and up to 100% FAME (B100) can be used, per EN 14214 [257], in engines certified for B100 fuels. Biodiesel has a 9% lower volumetric energy content than diesel fuel due to its oxygen content, and the fuel economy scales with this change in fuel heating value [3,243]. FAME biodiesels obtained from non-food crops, such as jatropha, camelina or algae, will have similar combustion and emissions characteristics as first-generation FAME biodiesels with similar fuel compositions, including the hydrocarbon chain lengths and saturation levels of the constituent mix of esters. It has been suggested that the environmental footprint of biodiesel production can be improved if bioethanol is used to transesterify the triglycerides of the oils to produce fatty-acid ethyl esters [8,9], but there could be an associated increase in fuel-production costs.

FAME biodiesels have cetane numbers between 48 and 65 [85,241]. At high-temperatures, the reactivity of long-chain esters is nearly indistinguishable for saturated and unsaturated esters [258], and ester reactivity shows little dependence on chain length [259], similar reactivity to alkanes such as n-heptane or n-decane [260,261], and a slight increase in reactivity for ethyl compared to methyl esters [262]. At low temperatures, long-chain esters have similar ignition properties to long-chain straight-chain alkanes [261], and these alkanes show little sensitivity to hydrocarbon chain length [239]. Addition of double bonds into the ester reduces the low-temperature chemistry and results in increased low-temperature ignition delay times and reduced cetane numbers [87,241], as found for hydrocarbon fuels [241].

FAME biodiesels have been shown to reduce engine deposits and coking compared to petroleum-derived fuels [5,247]. The reduced engine deposits are directly linked to the observed decrease in soot emissions for biodiesel compared to petro-diesel fuels, which has been explained by (i) the reduced local fuel-to-air ratio at the time of the initial fuel-rich flame ignition event, caused by the oxygen already present within the fuel [87,146,238], (ii) changes in the fuel–air mixing process due to the fuel physical properties; and (iii) the changes in the ignition propensity, or cetane number, of the fuel blend [3,5,7,87,146,243,245,247,249]. Fundamental laboratory measurements have shown that methyl and ethyl ester molecules produce lower soot than their alkane analogs [263,264], while butyl and pentyl esters can produce higher soot levels due to aromatic-formation reactions that occur during fuel pyrolysis [263]. The reduced sooting propensity of oxygenated fuels is directly related to the removal of carbon molecules from the soot-production radical pool due to their initial bond with oxygen [146]. However, these bonds also reduce the heat of combustion; thus Kholghy et al. found that FAME and alkane flames have similar soot concentrations and temperatures when both flames have the same energy input [265]. Methyl esters produce less soot than ethyl esters, an effect that is seen to reduce with increasing hydrocarbon chain length, and the presence of a double bond in unsaturated esters results in significantly higher soot formation [264]. The reduction in soot for biodiesel blends is also a result of the lower content of aromatic hydrocarbons in the biodiesel/diesel blend compared to neat diesel, since aromatic hydrocarbons are known to produce higher soot emissions than other fuel components [247,264]. Even though the total soot emissions may be lower, the particulate emissions from biodiesels can contain larger quantities of smaller nano-sized particles [243] that may have a significant impact on the resulting emissions toxicity [108].

NO_x emissions have been observed to increase for biodiesel compared to petro-diesel for many engine tests [5,7,242–253], while others have shown no increase or even a decrease for biodiesel (see discussion by Coniglio et al. [7]). The reason that no definitive explanation has been provided for the so-called "biodiesel NO_x effect" [250] is that it involves complex combustion and pollutant chemistry in the turbulent non-premixed flame that consumes the vaporized and partially-premixed diesel fuel within the unsteady turbulent flow of the engine cylinder [87]. It has been established that the following factors are important in determining whether a selected biodiesel, or any other alternative fuel, blend will show increased or decreased NO_x emissions in a specific diesel engine: (i) changes in flame composition and temperature that result from the effect that fuel physical properties have on the fuel delivery, spray, evaporation and mixing processes [5,244,248–250,252]; (ii) changes in flame temperature caused by variation in the local fuel-to-air ratio at the time of the initial fuel-rich flame-ignition event due to different fuel-oxygenation levels and cetane numbers [87,238,246,248,251]; (iii) increased flame temperatures, and associated increased production of thermal NO_x, due to reduced radiative heat losses caused by lower soot-production rates [238,244,248,251], even though biodiesels have lower energy content and, typically, lower adiabatic flame temperatures than petro-diesels [244]; and (iv) changes in the prompt-NO formation rate due to changes in fuel chemistry [6,242,266]. Fundamental flame experiments have shown that the methyl esters that make up FAME produce lower NO_x emissions than their alkane analogs under equivalent fuel–air stoichiometry, due to reductions in both thermal and prompt NO contributions [266]. These studies also show that unsaturated FAME fuel molecules produce more NO_x than saturated fuels, due to their higher flame temperatures, and that ethyl esters can be prone to slightly higher NO_x emissions, although the effect is small for esters with longer hydrocarbon chain lengths [266]. From these fundamental flame studies, it is clear that the "biodiesel NO_x effect" does not arise from any intrinsic fuel-chemistry issue but, rather, results from complex interactions between the various physical and chemical properties of the fuel on the performance of individual CI engines.

In order to reduce these NO_x emissions, several options are available. Optimizing the fuel injector timing, or adjusting other engine operational parameters, should allow the engine to be tuned to reduce NO_x emissions for a specific fuel mixture [6,243,245,246,250,253], although this will typically simultaneously increase the soot emissions due to the well-known tradeoff between soot and NO_x emissions [245]. Adjustment of the biodiesel blend cetane number through the use of additives is another option for legacy fleets [249] but the potential for this solution may be limited for advanced engines [250]. Use of exhaust-gas recirculation can greatly reduce NO_x emissions for FAME-diesel blends [246,249,250], but this can slightly increase soot emissions [253]. The use of modern engine control systems and low-temperature combustion processes to achieve low-emissions CI operation will be discussed further in Section 4.2.

Advances in the ability to model the combustion chemistry of these biodiesel fuels [7,86,241,242,267,268], including the development of reduced chemistry models [152,154], as well as improved modeling of the complex turbulent combustion environment in CI engines, will aid in unraveling the complex physical and chemical processes taking place in CI engines that lead to these various toxic pollutant emissions.

3.2.4. Renewable, synthetic diesel fuel effects on CI engine performance and emissions

One problem with FAME biodiesel is the poor oxidative stability of the fuel, especially for fuel molecules with more double bonds, and fuel polymerization can cause filter clogging [87]. Renewable

diesel fuel derived from either hydrotreating FAME biodiesel [73], or through FT synthesis [13,91,94], is more compatible with existing engine technology than FAME biodiesels and, thus, leads to improved engine performance [73,94]. These renewable diesel fuels have effectively-equivalent energy densities as petroleum-derived fuels, due to the lack of oxygen content and similar hydrogen-to-carbon ratios [91], and cetane numbers in the range of 70–75, so that the straight-chain fuel must be blended with lower quality fuels for use in legacy diesel engines [92], or be branched via oligimerization reactions to a cetane number around 50 for use as a pure diesel fuel [93]. FT fuels do not contain aromatic hydrocarbons and, thus, have poor lubricity characteristics, which can be remediated by blending FT synthetic diesel with FAME biodiesel or petroleum diesel [94], or by using specialized aromatic additives [96]. The high cetane number of FT or hydrotreated-renewable-diesel fuels and their lack of aromatic content are considered to be the primary factors responsible for the observed decrease in NO_x, soot, unburned hydrocarbon and CO pollutant emissions, and increase in thermal efficiency, observed for FT fuels compared to conventional diesel [73,94,252]. More details on the combustion properties of FT-derived fuels compared to petroleum-derived fuels are given for aviation fuels in Section 3.3.3, and the same discussion applies to using these fuels in either gas-turbine or diesel engines.

3.2.5. Alcohol–diesel blends for CI engines

Smaller oxygenated fuels, such as alcohols (e.g., ethanol or butanol), are not applicable as alternative diesel fuels in a pure form due to their high octane rating, which corresponds to a low cetane number, typically less than 10 [85]. The poor ignition properties of these fuels delays ignition and results in higher unburned hydrocarbon emissions [269,270]. Ethanol–diesel blends have been used, typically only up to a maximum of 15% due to solubility issues at low temperatures, and generally show reductions in sulfur-oxide and particulate-matter (soot) emissions, no change or slight reductions/increases in NO_x and CO emissions, and increases in unburned hydrocarbon emissions [269,270]. Higher CO levels are observed in partially-premixed ethanol flames than for hydrocarbon flames, and there is also a high sooting propensity for ethanol, due to the direct production of ethylene and other soot precursors during the initial fuel decomposition [210]. This is complicated by the fact that the carbon bonded to the OH functional group only contributes one half of a carbon to the soot-formation radical pool [146]. Droplet combustion experiments of *n*-butanol showed very low soot levels due to less acetylene production during the combustion process [271]. Blends of *n*-butanol with *n*-dodecane show a reduced sooting propensity for butanol, but also a lower rate of soot oxidation after it is formed that can slow soot burnout before exhaust [272], which could lead to higher net PM emissions.

Alcohols are ignition-retarding compounds when added to diesel fuel [176]. The reduction in low-temperature ignition propensity (lower cetane numbers) when alcohols are blended with petroleum fuels is caused by the alcohol acting as a sink of reactive species that reduces the overall chain-branching reaction rates and, thus, slows ignition [171,176], as discussed above in the context of the octane ratings. The high-octane *tert*-butanol has a highly-branched structure that results in it having the lowest reactivity, and hence smallest cetane number, of the butanol isomers, as well as a lower cetane number than ethanol [176]. Interestingly, even though it has the lowest pure-component cetane number with the largest variation from petroleum diesel, it has the least effect in retarding the ignition process of alcohol–diesel fuel blends of all of the alcohols studied [176]. This is due to the fact that the reactive-species-scavenging reactions discussed

above are less likely for the highly-branched *tert*-butanol molecule [176], so that it acts like an inert compound, rather than an ignition retarder, in the mixture. The combustion properties of alcohol fuels, or their blends with diesel, can be improved by adding ignition promoters, such as alkyl nitrates [273–276]. More research into the chemical mechanisms behind these ignition promoting additives and studies on engine performance and emissions are needed.

3.2.6. Pyrolysis liquids as fuels for CI engines

Pyrolysis liquids (PL) have been used within CI engines, but no study has resolved all the performance, emissions and durability issues. There has been some important prior work investigating the feasibility of operating boilers, gas turbines and diesel engines with PL [99]. In a 10 kW spray burner fueled by a blend of 80% PL and 20% ethanol by volume, the PL blend had higher CO, NO_x, and particulate emissions than number 2 fuel oil (i.e. diesel) while PL's emissions were more comparable to number 4 fuel oil because of their similar non-distillable fraction, fuel nitrogen, and ash contents [100].

Solantausta et al. first published a study on the use of PL in CI engines in 1993 [277], and since then there has been a number of engine studies in this field [101]. Several other investigators have studied the performance of PLs in CI engines with power outputs in the range of 5–550 kW [277,278]. The most common technical challenges encountered when fueling CI engines with PL are: poor ignition quality, injector needle, nozzle, or fuel pump corrosion and erosion, clogging of injectors, and coke deposition in combustion chambers [279,101]. In addition to these challenges, the properties of PLs are not ideally suited for combustion in CI engines. Specifically, PLs are acidic, contain organic solids, and inorganic ash particles, all of which contribute to the corrosion or erosion of engine components [280,281]. The low heating value, along with the high water content of PLs contribute to slower heat release, incomplete combustion, and in some cases, high CO emissions [279]. Other properties that affect the use of PLs in CI engines are the viscosity and surface tension of the liquid. These properties are both higher than the same properties for diesel fuel and therefore lead to poorer atomization within CI engine combustion chambers; however, these properties improve with increasing temperatures [281]. The poor atomization in turn leads to larger droplets being formed, longer ignition delay times, and coking on cylinder walls. Furthermore, it has been shown that PL combustion is kinetically limited, while diesel fuel is mixing limited. That is to say that PL fuels require more time (or higher chamber temperatures) for the chemical reactions to occur [280].

A number of methods to improve the performance of PL in CI engines have been proposed and tested. Several researchers have attempted to deal with the poor ignition of PLs by using ignition improver additives with high cetane numbers, such as di-ethyl-hexyl-nitrate or diglyme in quantities ranging from 5 to 10 wt% [280,282]. Another method of dealing with the poor ignition of PL is to raise the temperature within the combustion chamber, with the use of preheated intake air. Additionally, modification of the piston can be utilized to increase the compression ratio within the engine cylinder, which also increases the cylinder temperature. Van de Beld et al. has successfully modified the piston to increase the compression ratio from 17 to 22, which has the effect of raising the cylinder temperature and reducing the amount of air preheat [283]. Finally, diesel pilot injection has been used to ensure proper combustion of PLs in the cylinder, achieving sustained operation with high amounts of PL used [277,284,285]. Another method of increasing combustion stability in CI engines is emulsification of PL with diesel fuel [278,282,283,286–289]. While this has proven successful for achieving stable operation in CI engines, injection

systems still undergo severe corrosion. Methods for reducing the corrosion or erosion effects produced by the acidic nature or ash content in PL include material selection for the fuel injection system that are compatible with acidic liquids, such as stainless steels. As for clogging or solids formation in injection nozzles, researchers have attempted the use of inline fuel filters, pre-filtering the PL fuel, or solvent addition to the PL fuel prior to injection. These methods have been only partially successful, as most studies mention some instance of injector clogging, or deposit formation in the injection system [290].

In terms of the gas emissions from the operation of PL in CI engines, in general, the NO_x content is reported to be roughly half that of diesel NO_x emissions, while the CO emissions are reported to be as much as 12 times higher than diesel CO emissions [279]. Few studies measured unburned hydrocarbons (UHC or THC) or particulate matter (PM); however, it was shown that as engine loads increased the UHC becomes comparable or higher than that of diesel [290]. One engine study found that PL had both lower PM number concentration and size than when using diesel fuel [287].

Due to these various engine operation and durability issues, it is unlikely that raw PL is a feasible transportation fuel and upgrading will be needed to convert it into either a drop-in fuel or a blend additive.

3.3. Gas-turbine (jet) engine alternative fuels

3.3.1. Gas-turbine (jet) engine combustion process

In jet engines, liquid jet fuel is injected into the combustion chamber, which can be a more traditional array of cans around the axis of the engine or a modern annular combustor [291,292]. By its nature of operation, the gas turbine is a continuous-flow machine, rather than a cyclical machine like the internal combustion engines discussed previously. The combustion process and flame stabilization technologies vary with engine design, but a common flame stabilization approach in aviation engines is to employ an atomizing fuel injector coupled with a swirling airflow and a bluff body to provide a recirculation zone of hot combustion products that can act to stabilize the flame and prevent blow-off, or flame out [292,293]. As in CI engines, non-premixed flames are stabilized that result in high flame temperatures and, thus, high NO_x emissions, and produce soot due to high-temperature fuel-rich regions located on the fuel side of the non-premixed flame. In order to reduce the NO_x levels, a successful combustion strategy has been to use rich-quench-lean combustors [291,292,294,295], and Fig. 3 is a cartoon describing the general properties of such a rich-quench-lean gas-turbine combustor, inspired by the detailed simulation results of Mueller and Pitsch [291]. The non-premixed flame is stabilized using swirl and bluff-body recirculation, and the airflow to the combustion chamber is controlled so as to maintain a very fuel-rich mixture in the primary rich flame zone [291,292]. The lack of excess oxygen and the relatively low flame tempera-ture of the fuel-rich mixture in the primary combustion zone reduces the formation of thermal NO_x [296], since only the periphery of the rich primary zone will react at stoichiometric conditions with the available cooling air. Following the primary rich combustion zone, a high flow rate of air is provided to quench the flame and reduce the overall equivalence ratio of the mixture from fuel-rich to fuel-lean conditions [292,296]. The partially-oxidized fuel remaining in the mixture is fully oxidized to combustion products in a distributed turbulent reaction zone downstream of the quench zone [291], termed the lean dilution zone [292,296]. Mueller and Pitsch have shown, via detailed simulations of a Pratt and Whitney combustor, that a large volume of soot is formed in the fuel-rich primary zone, which is mostly oxidized by the quenching and dilution air [291]. The resulting soot emissions from such a rich-quench-lean combustor occur due
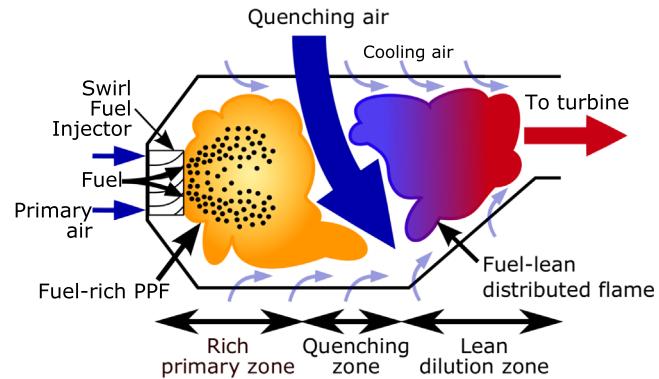
Fig. 3. Cartoon of the combustion process in a rich-quench-lean gas-turbine combustor. The jet fuel is atomized into a swirling and recirculating flow at the swirl fuel injector and the airflow is set so as to keep the primary flame zone fuel rich. A large amount of air is injected after the primary rich flame zone to quench the reaction and create a fuel-lean mixture, which then reacts in a distributed and well-stirred reaction zone within the lean dilution zone.
Cartoon inspired by numerical simulation results presented by Mueller and Pitsch [291].

to pockets of fuel-rich mixture that escape through the quenching and dilution zones without being mixed with excess air and, therefore, the soot is not oxidized in the lean dilution zone and escapes the combustor into the turbine and engine exhaust intermittently as "puffs" of smoke [291].

3.3.2. Jet fuel combustion properties

Jet fuel [54], or aviation kerosene, is a mix of hydrocarbon molecules that includes, among others, straight-chain paraffins (*n*-alkanes), cyclic paraffins (cyclo-alkanes), branched-chain paraffins (e.g., *iso*-alkanes), and aromatic molecules [53]. It is a middle-distillate cut of crude oil that falls between gasoline and diesel fuel [297]. Researchers have proposed various surrogate fuels for jet fuel, typically containing mixtures of normal alkanes, such as *n*-decane or *n*-dodecane, cyclo-alkanes, such as methyl-cyclo-hexane or *n*-propyl-cyclo-hexane, branched alkanes, such as *iso*-octane, and aromatics, such as toluene, xylene or *n*-propyl-benzene [145,298–300]. Recent work by a multi-university research team has proposed surrogate mixtures of *n*-dodecane/*iso*-octane/toluene (42.67/33.02/24.31% by mole) [301] or *n*-dodecane/*iso*-octane/1,3,5-tri-methyl-benzene/*n*-propyl-benzene (40.4/29.5/7.3/22.8% by mole) [150] that capture Jet A fuel properties over a wide range of combustion conditions, ranging from low-temperature ignition to high-temperature flames. Recent work has shown that similar perfor-mance can be achieved by blending representative distillation cuts of real gas turbine fuels [302]. Combustion models for such jet fuel surrogates have been proposed [299,300,303–305], including reduced models e.g., [306] and model validation is ongoing [148,156,298,300,303,305,307,308].

3.3.3. Biojet fuel effects on jet engine performance and emissions

Serious concerns have been raised regarding the use of FAME biodiesel fuels in aircraft due to the poor cold-temperature properties of these fuels and the low temperatures the jet fuel is exposed to during aircraft flight at high altitudes [309]. For that reason, the jet fuel standard (D1655-09) was modified to limit the amount of FAME in aviation fuel to 5 mg/kg (5 ppm), and FAME is now considered to be a contaminant in the jet fuel delivery infrastructure [53,309]. The recent standard (D1655-13) states that FAME is "not approved as an additive for jet fuel" and that the industry is "currently applying the additive approval process to evaluate the possible allowance of the presence of up to 100 mg/kg of FAME in aviation turbine fuel to facilitate the distribution of

aviation turbine fuel in systems containing multiple products" [54]. The consensus in the aircraft industry is that any proposed biofuel or alternative fuel for aviation must be a drop-in fuel; in other words, the new fuel must match all of the fuel properties of aviation jet fuel (D1655 [54]) and be completely compatible with existing infrastructure and engines. Therefore, if vegetable oils, animal fats, or other oxygenated biofuels are to be used as a feedstock for aviation fuel, the oils must undergo hydrotreatment and upgrading to create what is known as hydrotreated renewable jet (HRJ) fuel [53,309], sometimes also called hydro-processed esters and fatty acid (HEFA) fuels, e.g. [56], which is similar to renewable diesel obtained from hydro-deoxygenation of bio-diesel [73]. In addition to the cold-temperature issue discussed above, any oxygen content in aviation fuel would reduce its volumetric and mass energy densities, reducing vehicle range and the efficiency of the fleet [310]. Therefore, in this review, only drop-in synthetic-hydrocarbon biofuels are discussed for aviation applications.

Both HRJ and FT-derived biojet fuels, often also termed synthetic paraffinic kerosene (SPK), are composed of straight- and branched-chain paraffin molecules. SPK fuels, derived from specific feedstocks and conversion processes, may be blended up to 50% with petroleum jet fuel according to the ASTM D7566 standard [55,309]. One major issue with these fuels is their lack of aromatic content, because the aromatic molecules in the fuel help the seals to swell, preventing them from drying out and shrinking which could result in fuel leakage [53,95,96,309]. Therefore, the aromatic content in any biojet/jet fuel blend is fixed at a minimum of 8%, which is the historical minimum of aromatic content in aviation jet fuel, even though no scientific evidence for the necessary aromatic content has been obtained [53]. Aromatics can be produced from catalytic fast pyrolysis of biomass-derived feedstocks, which suggests the possibility of a fully-renewable jet fuel [36,311], and the most-effective additives for seal-swell enhancement will be small aromatic molecules with significant polarity and hydrogen-bonding potential [96]. Importantly, the reduced aromatic content of HRJ or FT biojet fuels is also an advantage, as increased aromatic content is associated with poorer combustion efficiency (increased CO and unburned HC emissions) and increased soot emissions [53,145]. Indeed, use of synthetic jet fuel from FT or HRJ processes has been shown to reduce NO_x and soot particulate emissions, reduce CO emissions in some cases, and to reduce fuel burn and, thus, improve fuel efficiency in aviation engine tests [53,95]. The improvement in fuel efficiency is due to the increased energy content of the paraffinic FT or HRJ fuels compared to the aromatics that make up a significant portion of Jet-A [53]. Fundamental laboratory experiments have recently shown a reduction in peak soot concentrations by approximately a factor of 4 between Jet A-1 (28% aromatics) compared to either n-decane or a SPK fuel, which were similar, due to the lack of aromatic hydrocarbons in the SPK or alkane fuels [312,313].

The combustion properties of the synthetic hydrocarbons that make up FT or HRJ fuels are very similar to that of traditional petroleum–fuel components, and thus modeling of the combustion of biojet and jet-fuel blends can be accomplished with a similar number of surrogate components as for jet fuels [156,157,314,315]. The flame propagation speeds of HRJ and FT biojet/jet blends are found to be very similar to that of traditional Jet A and hydrocarbon surrogate molecules [307,315–323]. This is consistent with our understanding of high-temperature combustion, as it is now widely understood that the flame propagation speed is not sensitive to the hydrocarbon chain length; for example, the flame speeds for alkane fuel molecules with greater than 5 carbon atoms all collapse together when plotted as a function of the normalized fuel–air equivalence ratio at consistent initial temperatures and pressures [148]. These biojets have

reactivities between that of a more-reactive straight-chain alkane fuel, such as n-decane, and a less-reactive aromatic fuel, such as toluene [156,307,315]. Consistently, fuels with lower levels of aromatic content, and correspondingly higher concentrations of straight-chain, branched or cyclic paraffins, will have slightly higher flame speeds and are more resistant to extinction than those with higher levels of aromatics [316,319,320].

While premixed combustion properties are important for understanding reactivity changes between different fuels or fuel blends, traditional aviation gas-turbine engines operate using non-premixed combustors that have some similarities to CI engines (cf. Figs. 2 and 3); the combustion is sensitive to fuel spray and vaporization processes, as well as non-premixed turbulent combustion and flame extinction. Biojet fuels must have similar vaporization properties to Jet A to meet specifications [54,55], generally exhibiting higher vapor pressures at the same temperature [315], which should be beneficial for cold-start and re-light at altitude. Indeed, re-ignition of the engine at altitude after a flame-out event is an important safety issue. Current synthetic fuels have been shown to have similar ignition performance as Jet A-1, provided there is a sufficient fraction of light hydrocarbons in the fuel that can vaporize and form the initial flame kernel around the spark region [324]. Successful transition of the resulting flame kernel into a fully-burning condition depends on the local turbulence intensity and mixture composition [325]. Ignition of heavier fuels, such as diesel, requires higher overall fuel–air ratios, or higher fuel spray rates, in order to increase the fuel vapor composition in the near-spark region so as to achieve successful ignition [324].

Once the engine is ignited, the steady-state non-premixed flame temperatures will scale with the adiabatic flame temperatures of a stoichiometric fuel–air mixture, and the effect of the turbulent flow within the gas-turbine engine combustor on these flames can be assessed through the non-premixed flame extinction behavior of these fuels. Biojet fuels show similar non-premixed flame extinction characteristics to Jet A, with flames becoming more difficult to extinguish as the level of biojet increases, or the level of aromatics decreases, in the biojet/jet blend [315]. Non-premixed flame extinction conditions have been shown to be more sensitive to the diffusivity of the fuel molecule, and hence the hydrocarbon chain length or molecular mass, than premixed flame properties [317,318]. Addition of toluene, or other aromatic compounds, is seen to increase the extinction propensity of paraffin–aromatic blends compared to the paraffins alone [319,326], due to a kinetic coupling that reduces the concentration of reactive OH radicals within the flame zone via H-abstraction reactions with the more-chemically-stable aromatic fuel [326]. The impact of different fuel blends on their non-premixed flame extinction properties has been explained by using a radical index, which relates the production of OH radicals for the fuel blend of interest to a reference fuel, such as n-decane, and the transport-weighted enthalpy flux into the flame, which is proportional to the product of the bulk fuel concentration, the fuel diffusivity (inversely proportional to the square-root of the fuel molecular weight), and the heat of combustion of the fuel [326,327]. The correlation proposed by Won et al. [327] fully accounts for the differences in non-premixed flame extinction for a wide range of jet fuel surrogate components.

Low-temperature ignition studies show that HRJ fuels ignite more readily than the Jet A fuels due to their higher cetane numbers [308,328], and higher levels of branching in the fuel lead to reduced low-temperature reactivity as does inclusion of cyclo-alkanes [329]. Under high-temperature ignition conditions, FT fuels collapse onto results for Jet A [328,330], consistent with the observed lack of sensitivity of high-temperature ignition of long-chain alkanes to the hydrocarbon chain length [239,331] and

the collapse of the high-temperature flame speeds [307,315–321]. Other studies, based on flow reactors at low temperatures, ignition delay times, and extinction of laminar flames show that FT synthetic jet fuels can be modeled by a surrogate of *n*-decane and *iso*-octane [314].

The similar reactivities of these biojets compared to Jet A, along with their reduced aromatic content, explains why the fuel combustion performance and emissions of these fuels in practical engine geometries is improved compared to the Jet A baseline, especially in terms of soot, carbon monoxide, and unburned hydrocarbon emissions, as is observed in engine tests [53,95,332]. There appears to be no technological reason that would prevent synthetic and bio-derived fuels from becoming 100% replacements for petroleum jet fuel but, rather, cost is likely to remain the critical factor limiting biojet fuel penetration.

4. Alternative propulsion technologies for transportation vehicles

The modern vehicle has been optimized in terms of its production cost and to meet increasingly stringent pollutant-emissions standards, rather than for its fuel efficiency per se. As the price of fuel increases due to supply-demand constraints, it is expected that increased attention will be paid to reducing operational costs through improved fuel efficiency. Hybrid-electric vehicles represent one important way to improve the overall performance of the powertrain, because significant benefits are obtained by (i) using regenerative braking to capture and store the vehicle's kinetic energy in the battery for later use, (ii) avoiding engine idle and (iii) allowing the engine to operate at its optimal set point [333]. While fully-electric vehicles are coming onto the market, the reduced vehicle range that results from the low energy density of current batteries prevents their widespread adoption. Another important goal in advanced engine design is to lower pollutant emissions to meet increasingly stringent regulations and improve urban air quality. As discussed previously, keeping the fuel–air mixture to fuel-lean or near-stoichiometric conditions can avoid the soot formed in fuel-rich mixture regions, and lowering the combustion temperature can reduce NO_x emissions. Thus, advanced engine designs are aiming to use low-temperature premixed or partially-premixed combustion [234], similar to the flameless oxidation [334] or MILD combustion [335] processes used in industrial burners, in order to meet ultra-low-emissions standards. Several potential future engine technologies, ranging from near-term to far-term solutions, are discussed in the following sections.

4.1. Homogeneous-charge compression-ignition (HCCI) engines

Gasoline engines suffer from reduced efficiency at partial load, because of throttle-valve losses, and are limited to lower compression ratios, resulting in lower efficiencies, than CI engines due to the potential for engine knock [122–124,170,229]. A novel engine concept, that is a cross between traditional spark-ignition (SI or gasoline) and compression-ignition (CI or diesel) engines, is the homogeneous-charge compression-ignition (HCCI) engine [121,123,126,131,170,336], which achieves high efficiency through the removal of the throttling valve [230] and through the use of high compression ratios as in diesels [170,229]. HCCI combustion also results in lower combustion temperatures, which reduces heat losses to the engine cylinder walls and thereby improves engine efficiency and vehicle mileage [2]. One limitation to HCCI engine performance is the fact that combustion becomes unstable under high-load conditions, due to fast pressure rises resulting in engine noise, knock and potential engine damage, while

auto-ignition is difficult to control under low-load conditions due to the low fuel concentrations [124]. Therefore, HCCI engines cannot cover the full operational range needed by a typical passenger vehicle [124,170]. One solution for operation at low-load conditions (e.g., engine idle), is to create a stratified charge within the cylinder using direct injection to maintain a sufficient fuel–air ratio next to the spark to enable spark ignition, similar to the DISI engine discussed in Section 3.1.5 [122,124]. At high loads, dilution of the fuel–air mixture with additional exhaust gases, either by employing external exhaust-gas recirculation (EGR) or variable valve timing to trap exhaust within the cylinder before the air is ingested, can limit the heat-release rate and pressure rise to prevent engine knock [124]. Concerns about the need to switch the engine between the DISI mode at low loads to lean-burn HCCI mode at mid loads and to a EGR-diluted fuel-rich HCCI mode at high-loads [124], can be eliminated if HCCI engines are used as a generator, or are supplemented with electric boost, within a hybrid-electric powertrain [170].

A cartoon of the HCCI combustion process is given in Fig. 4 [87,121,229,337]. HCCI engines utilize a premixed fuel-and-air charge in the engine, similar to SI engines, but no spark is utilized and ignition is induced solely through gas compression resulting from piston motion. The fuel–air mixtures in the engine are too fuel-lean, or too diluted with exhaust gases, to support a flame and the ignition of the gas happens in many small "hot spots", or "ignition kernels" distributed throughout the engine, a process controlled by the low-temperature combustion chemistry [87,121,123,170]. The initiation of low-temperature combustion throughout the cylinder, instead of a spark initiating a high-temperature flame as in SI engines, allows extremely low fuel–air ratios to be utilized which can reduce the engine temperatures and, therefore, NO_x emissions. Unfortunately, HCCI engines can be noisy and emissions of unburned hydrocarbons and carbon monoxide can increase due to fuel remaining trapped in crevices in the piston and cylinder, and because the low combustion temperatures reduce the burnout of CO to CO_2 [112,123,124,126,131]. These problems are exacerbated by cold initial engine temperatures, making cold start in the winter months problematic [123]. In order to burnout the hydrocarbons and CO, a combustion temperature
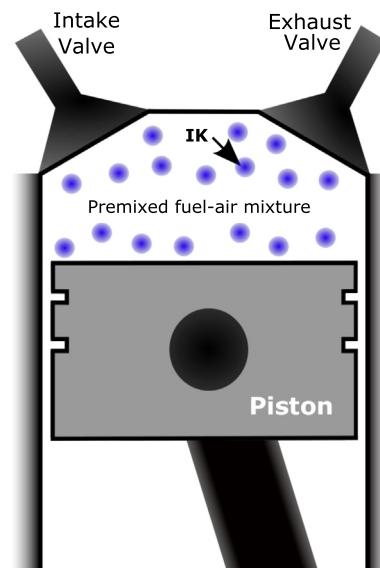
Fig. 4. Cartoon of the combustion process within a HCCI engine. A premixed fuel–air mixture is created within the cylinder that is either fuel lean, i.e. diluted by excess air, or diluted with exhaust gases. Auto-ignition of the mixture occurs in multiple hot spots, or ignition kernels (IK), and the combustion process occurs as a low-temperature distributed reaction, rather than as a propagating flame. Cartoon inspired by figures in Refs. [87,121,229,337].

higher than 1500 K is needed, while temperatures above 1800 K should be avoided to prevent NO_x [170]. Soot formation is generally low due to the fuel-lean mixtures used; thus, one benefit of HCCI engines is that they can achieve the efficiencies associated with CI engines at very low emissions levels, which can be dealt with using current, relatively inexpensive, exhaust after-treatment technology [170].

No direct ignition-control mechanism exists in HCCI engines like the spark in a SI engine or the fuel-injection timing in a CI engine and, thus, low-temperature combustion chemistry controls ignition and has a strong influence on engine stability [123,170,336]. Control strategies relying on exhaust-gas recirculation (EGR), fuel and temperature stratification within the cylinder, and other techniques are being employed [123,170], and further knowledge of the low-temperature combustion chemistry of possible HCCI fuels, including biofuels, are needed for modeling and design of these devices [126,131,132,170]. The ideal HCCI fuel is one with a medium octane rating, but this depends on the compression ratio and the mixture charge within the cylinder [123,170]. n-Butanol has been used as an HCCI fuel both neat [338] and in blends with gasoline, where both formaldehyde and acetaldehyde emissions significantly increase compared to gasoline [339]. Recent studies have shown that addition of butanol to primary reference fuels retards ignition timing [340], consistent with the octane rating of the fuel, while other experiments found that ignition timing was advanced for butanol–gasoline blends [339].

It has been suggested that the fuel chemistry should be optimized in order to control the combustion event, or to vary, in real time, the fuel blend between different fuel types to control the ignition within the engine [336], such as high-octane ethanol and low-octane diesel, as in the reactivity-controlled compression-ignition (RCCI) engine variant of HCCI [87,170,341]. Studies of ethanol and n-heptane mixtures in a HCCI engine showed that addition of the highly-reactive n-heptane could have a strong effect on the heat release rates and combustion timing of the blend [342]. It is also possible to achieve ignition control in HCCI engines through the utilization of two fuel injection pulses into the cylinder: the first injection is at the end of the exhaust stroke so as to reform the fuel into reactive intermediates using low-temperature cool-flame combustion reactions [343], while the second fuel-injection event is during the intake or compression stroke [170]. Varying the amounts of fuel injected into the two pulses, and their timing, can alter the overall reactivity of the final cylinder charge and control the resulting combustion phasing [170]. As more EGR and fuel stratification are used in HCCI engines at high loads, the lines are blurred between HCCI and low-temperature-diesel combustion modes [170], as discussed further in the next section.

It is anticipated that efficient HCCI combustion would require a tightening of fuel property specifications, compared to those for current gasoline fuels, and for more than one type of fuel in the RCCI variant. It appears that an optimum fuel for HCCI operation would have auto-ignition properties between that of gasoline and diesel fuels [2]. While oxygenated biofuels could play a role as ignition-control additives, or as secondary RCCI fuels, it appears that HCCI engines would primarily require either petro-fuels or synthetic hydrocarbons from FT or hydrotreated oils. These fuels would need to be processed via oligomerization reactions to control the fuel branching, and hence ignition properties, of the fuel. Such fuel-upgrading reactions require energy and hydrogen inputs that will likely increase the net life-cycle greenhouse-gas footprint of the resulting HCCI/RCCI-specific fuel. These low-temperature combustion engines have shown fuel-efficiency improvements of approximately 20% over standard CI engines, and 40–50% over conventional SI gasoline engines [2], which warrants further efforts to improve the internal combustion engine even after more than a century following its development.

Another potential method to control reactivity and auto-ignition in a HCCI engine is to employ plasma sources to activate the chemical mixture and effect the ignition delay times [344–351]. Employing plasma activation in SI engines leads to reductions in the lean limit of engine operability [345,352] which could provide an opportunity to run an engine in a mode that falls between HCCI and traditional SI or DISI operation.

4.2. Low-temperature combustion compression-ignition (diesel) engines

In order to simultaneously reduce the production of NO_x and soot emissions in CI engines, it is possible to use highly-diluted combustion conditions to keep the flame temperature below the critical value of 1650 K [229,336]. Such low-temperature diesel combustion systems rely on exhaust-gas recirculation (EGR), at dilution levels of greater than 60%, to reduce the oxygen content to below 10% in the intake charge, i.e., the exhaust-product/air mixture drawn into the cylinder before compression and fuel injection [229,336]. By intentionally lengthening the ignition delay time of the fuel–air-exhaust mixture through dilution via EGR and by utilizing multiple high-pressure fuel injection events, each resulting in highly-turbulent jets that promote rapid mixing, a more homogeneous mixture is obtained that will burn in a premixed or partially-premixed mode, distributing the reaction zone spatially and reducing the flame temperature as in HCCI engines [123,170,229]. Thus, there is a spectrum of possible engine in-cylinder conditions, varying from traditional non-premixed diesel operation, through partially-premixed and stratified engine charges, to fully-premixed HCCI mode, that can be created by the combustion engineer to control the local and global mixture compositions at ignition and combustion, which strongly affects the resulting combustion temperatures and the associated pollutant emissions. Such control of the engine charge composition is possible through varying the fuel injection timing, including multiple pulses, and its location, which can be within the intake port or from multiple in-cylinder fuel-injectors [229]. A cartoon of one possible diesel low-temperature combustion process is provided in Fig. 5 [123,229,353,354].

More premixing of the fuel–air-exhaust mixture reduces soot emissions and the lower resulting flame temperatures reduce NO_x emissions [110,229,237]. Unfortunately, these reductions in NO_x and soot come at the expense of increased unburned hydrocarbon and CO emissions, which also result in reduced thermal efficiency of the engine [336]. Current development efforts on low-temperature combustion systems aim to address these deficiencies and improve the thermal efficiency and emissions characteristics of advanced CI engines. Such efforts increasingly demand improved knowledge of, and models for, the fundamental combustion chemistry of a range of potential alternative diesel fuels, as well as an improved understanding of the turbulent mixing and heat transfer processes within the engine cylinder.

The optimal fuel for low-temperature CI engines will likely be a low-cetane number fuel [355], or one with a mid-octane rating, to delay ignition until sufficient fuel–air mixing can occur. It is anticipated that these engines will place increased restrictions on the allowable biofuel/petro-fuel blend properties. As the operational modes of advanced diesel and HCCI engines move closer together [170,355], so will the fuel requirements of each engine, perhaps leading someday to a single, relatively tight, fuel specification for a variety of low-temperature combustion engines.

4.3. External-combustion engines

In the future, the increased electrification of ground-transportation vehicles with hybrid-electric powertrains will reduce the need for high-power engines that can rapidly shift
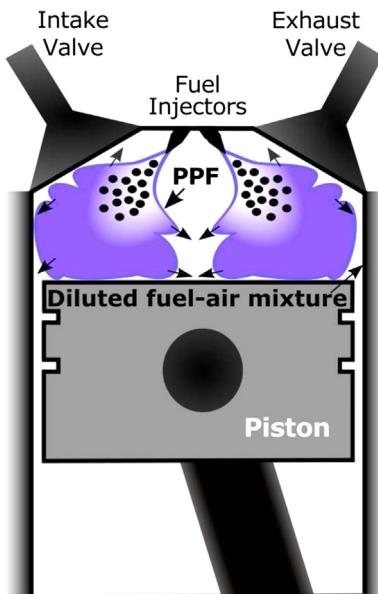
Fig. 5. Cartoon of a low-temperature diesel combustion process. Higher levels of premixing of the fuel with air and exhaust gases reduces the flame temperatures to reduce the formation of both soot and NO_x emissions. The partially-premixed flame (PPF) will typically be longer and broader than in a traditional CI engine because of higher levels of premixing. The flame is blue colored due to chemi-luminescence from formaldehyde, CH and other species, and because there is no soot formed to incandesce [123,229].

Cartoon inspired by images presented in Refs. [123,229,353,354].

from idle to full-power mode. The use of electric motors to drive the wheels in a series-hybrid vehicle converts the combustion engine into a range-extending device, where the motor runs at an optimal steady state and the shaft power is converted to electricity by a generator. The fact that the engine no longer needs high performance in terms of power, torque, etc., allows it and the gearing to be tuned so that the engine operates at a high-efficiency state and provides an optimal power level for the generator, thereby maximizing the efficiency of converting the chemical energy within the fuel to motive energy (power). When such a vehicle powertrain is envisaged, the current SI or CI internal-combustion engines do not necessarily provide the optimum performance. External-combustion engines, such as engines based on the Rankine or Stirling cycles, could potentially reach higher efficiencies, lower total emissions and provide quieter operation than traditional IC engines [356–358], but have not gained wide-spread acceptance due to high costs, low torque and poor response to load changes [359,360]. As discussed above, the torque and load response are not a factor when the external-combustion engine is coupled directly to an electrical generator, making such engines possible candidates for future hybrid-electric vehicles.

One issue with such engines is that combustion takes place externally to the engine and, thus, the thermal energy after combustion cannot be extracted for shaft work as effectively as it is during the expansion process within an internal combustion engine. In external-combustion systems, a significant amount of thermal energy can be lost through the exhaust products, which would nominally leave the vehicle at the high temperature associated with the hottest part of the heat engine. A typical external-combustion engine input temperature is somewhere around 1000–1400 K to maximize thermal efficiency while pre-venting engine damage or excessive parasitic heat losses, e.g. [361]. In order to reduce the loss of thermal energy in the exhaust, heat-recirculating burners transfer heat from the hot exhaust to preheat the cold reactants and provide an excellent means of concentrating the thermal energy in the region where heat is

extracted by the engine so as to improve the overall thermal efficiency [234,359,361–367]. Such burners could also be used for smaller-scale power generation [368,369], and can also allow control of the peak flame temperature in order to match this to the requirements of the engine and reduce excess NO_x formation [356,362,363,366]. Reduction of the fuel–air equivalence ratio to leaner conditions while maintaining the same peak combustor temperature through heat recirculation reduces unburned hydro-carbons and other pollutant emissions [362]. A cartoon of the type of combustion process involved in a heat-recirculating burner coupled to an external-combustion (Stirling) engine is provided in Fig. 6 [362,370,371].

Heat-recirculating burners extend what can be defined as a fuel due to the extension or near-elimination of flammability limits [362,366,372]. The use of heat-recirculation within a porous reactor allows combustion at extremely low equivalence ratios or with very-low-energy-content fuels, resulting in low NO_x exhaust emissions [362,364,365,373]. Similar gains can be achieved with counter-flowing streams of reactive mixtures separated by heat-conducting walls [362,366,374], such as the swiss-roll burner [362,363,368,372,374] or the counter-flow heat-exchanging bur-ner [362,374,375]. Recent work has shown that the flames in such burners stabilize through ignition at the locally-high wall tem-peratures within the excess-enthalpy zone and that flame stretch-ing can significantly increase the flame stabilization over a wider range of firing rates, allowing further fuel-flexibility or variability in the power output, as well as showing that 2-D effects can hinder the flame stabilization for very small channels [370]. More work is needed to understand the effect of a heat load, into the
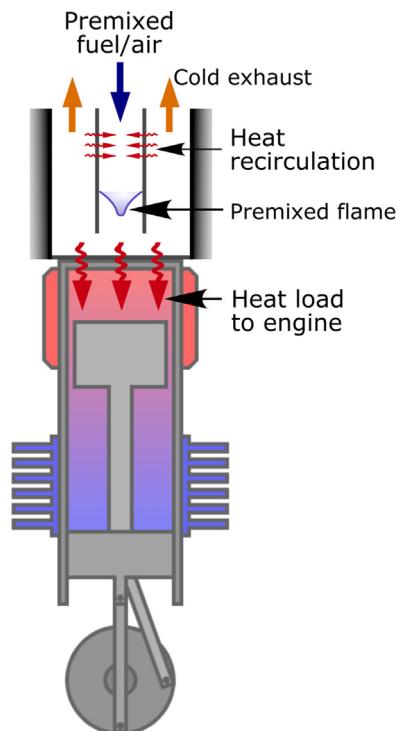
Fig. 6. Cartoon of a heat-recirculating burner coupled to a Stirling engine. Cold fuel and air is premixed and is preheated by the hot combustion products, reducing their temperature and thus reducing the thermal energy loss in the exhaust and increasing the thermal efficiency of the burner. The heat recirculation can improve the flame stability of a flame stabilized within the burner. An actual burner would likely require many relatively small channels, as opposed to the single flame channel depicted here, in order to provide a sufficient heat load to the engine. Heat is extracted from the hot combustion products to the external-combustion heat engine, which can achieve high thermal efficiencies.

Cartoon of burner design inspired by Ref. [362], flame shape inspired by numerical simulations from Ref. [370], and Stirling engine image obtained from Ref. [371].
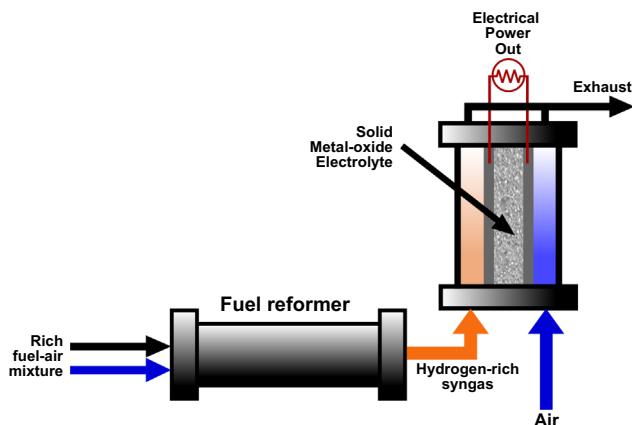
Fig. 7. Cartoon of a fuel-reformer and solid-oxide fuel cell. The fuel reformer partially oxidizes a fuel-rich mixture and produces a hydrogen-rich syngas that is, subsequently, oxidized in the solid oxide fuel cell by oxygen ions transported through the solid metal-oxide electrolyte. Electrical power is produced by the ion flow and can power a hybrid electric vehicle.

Fig. 8. Cartoon of an axially-staged premixed low-emissions gas-turbine combustor. The pilot flame is stabilized within a swirl flow after the fuel is rapidly mixed with air, resulting in a fuel-lean premixed pilot flame. The bulk of the fuel is burned in the primary flame zone, which is again formed after rapid premixing the fuel with air to prevent auto-ignition into the premixer. The primary flame is diluted and preheated by the combustion products of the pilot flame, which allows a flame to be stabilized at lower fuel–air ratios and, thereby, reduces flame temperatures and NO_x emissions. Soot emissions are greatly reduced due to the rapid premixing of fuel and air and avoidance of high-temperature fuel-rich zones.
Cartoon inspired by figures in Ref. [296].

engine, on such burner designs. It may also be possible to use low-temperature flameless oxidation [334] or MILD combustion [335] to simultaneously improve combustion efficiency and reduce pollutant emissions in such systems, similar to the low-temperature combustion approaches being used in advanced HCCI and low-temperature-combustion CI engines, and more work is needed in this area.

Heat-recirculating burners are inherently fuel-flexible by their design [365,376]; they have the ability of stabilizing a wide range of different fuels within the same geometry by optimizing the fuel and air feed rates for each different mixture. Fuel flexibility will allow the optimum, i.e., cheapest and cleanest, fuel source to be used at any given time. The cleanest fuel will be the one with the lowest total life-cycle pollutant emissions, including greenhouse gases. Lower life-cycle greenhouse gas emissions should, generally, correlate with lower levels of fuel upgrading for the same feed-stock, since upgrading typically involves addition of energy and/or hydrogen to the process that, currently, have associated carbon footprints. In an energy- and carbon-constrained world, improvements in ultra-low-emissions combustors and high-efficiency heat engines could provide considerable savings over incremental improvements in biomass-to-biofuel conversion efficiency.

4.4. Fuel cells

If the purpose of the engine in advanced ground-transportation vehicles is simply to convert chemical energy to electric power (energy), then a direct conversion through the use of a fuel cell can possibly lead to higher efficiencies, and lower pollutant emissions, than the combustion processes within internal- or external-combustion heat engines. Traditional polymer-electrolytic-membrane (PEM) fuel cells require pure hydrogen as a fuel and, therefore, have not achieved significant market penetration due to the fact that no widespread hydrogen refueling infrastructure exists and because of the low volumetric energy density, and safety concerns, associated with hydrogen transport and storage. More advanced solid-oxide fuel cells make use of both hydrogen and carbon monoxide as fuels and, thus, can operate on a wide variety of hydrocarbons, which typically need to be reformed either internally to the cell [166,295] or upstream of it to generate the necessary hydrogen and carbon monoxide syngas mixture required by the fuel cell [22,163,164,295,343,377–380]. A cartoon of a fuel-reformer and fuel-cell power system is given in Fig. 7.

Therefore, fuel-flexible reformer technologies could enable a wide variety of hydrocarbon-containing fuels to be used on a fuel cell vehicle [295,379,380]. Optimization of the reformer temperature, pressure and fuel-and-air feed rates might be needed if the fuel composition changed radically, but such systems could be much more fuel-flexible than vehicles operating on traditional SI and CI engines, or advanced HCCI and low-temperature-combustion CI engines. The fuel reformers can either involve the exothermic partial oxidation of the fuel, as would occur internally to the cell, or endothermic steam reforming in a, typically catalytic, reactor upstream of the cell, or a combination of the two reactions [164,379]. Such reformers could rely on heat-circulating burners [164,362,363,373,374,380,381], catalysts [164,379,382,383], and plasma-assisted combustion devices [164,345,382–384], or a combination of these technologies [383], to optimize their performance.

4.5. Advanced low-emissions gas-turbine (jet) engines

For aviation propulsion, the gas-turbine engine will remain the key propulsion technology due to its established safety record and high power density [294]. In order to meet future pollutant-emissions regulations that will likely be imposed upon next-generation engines, advanced low-emissions combustor technologies will be needed. As with the transition from traditional to low-temperature CI engines, advanced gas-turbine combustors will employ higher levels of premixing and dilution with excess air and exhaust gases in order to reduce emissions, since soot can be eliminated for premixed flames and the NO_x emissions scale strongly with flame temperature [107,295]. One potential approach demonstrated to date is the use of piloted and staged combustion [107,295,347], as in the twin annular premixing swirler (TAPS) burner [296,385–387]. A greatly simplified cartoon of such a staged combustion system is provided in Fig. 8. A fraction of the fuel stream is burned with air in a premixed pilot flame that is stabilized by a swirl burner and operates at fuel-lean, but relatively high-temperature, conditions. The main fuel and air flow are mixed rapidly with cyclone technologies in a primary swirl burner that stabilizes the primary flame. This flame is partially or technically premixed due to the high turbulence upstream of the flame zone and is both stabilized and diluted by the entrainment of hot combustion products from the pilot flame zone [107,295]. The premixing, preheating and dilution of the mixture greatly reduces soot emissions and allows flame stabilization in the primary flame at leaner conditions than otherwise possible, thereby reducing flame temperatures and NO_x emissions

[294,296]. Such staged combustion systems can also reduce the engine power during cruise by shutting off the fuel flow to some primary flame zones, maintaining combustion stability in the other burners by eliminating the need to reduce the flow to all combustors equally [294].

The combustion process in the diluted primary flame is strongly affected by its entrainment of hot, vitiated air and combustion products from the pilot flame [295,296]. The reduced oxygen content and elevated temperatures of the mixture decrease the auto-ignition time of the mixture [294] while also increasing the characteristic time of flame propagation. Recent experiments have shown how auto-ignition and turbulent flame-propagation processes can interact to affect the overall combustion rate, leading to a combustion process that varies spatially from a thin premixed flame to a low-temperature ignition flame to a well-stirred distributed reaction zone regime [347,388]. As discussed for CI engines, the low-temperature chemistry that is important for auto-ignition of aviation fuels is sensitive to the fuel composition and, therefore, advanced lean-premixed gas-turbine engines will be quite sensitive to the combustion properties of the alternative aviation fuels, including the cetane number [388].

Indeed, such lean-premixed combustion strategies appear to require tight tolerances on the fuel properties in order to ensure emissions compliance [295]. Ignition of these advanced combustion systems will also be more sensitive to the fuel vapor pressure and combustion properties, since the spark kernel has a smaller amount of fuel locally available, due to the fuel-lean operation as compared to traditional fuel-rich systems, to vaporize and ignite [324]. Using a premixed combustion process can also lead to complex acoustic interactions between the flames and the combustor dynamics, potentially leading to catastrophic failure [296,389,390]. Additionally, flashback of the flame into the pre-mixing chamber can result in significant engine damage and is an area of active research [391–393]. As a result of these various factors, future low-emissions lean-premixed engine designs may actually require a narrower fuel specification compared to the current ASTM fuel specification [54]. In order to provide fuel-flexible engine operation, or enable a broader jet fuel specification than at present, ignition problems and combustion instabilities would need to be eliminated through combustor control technologies [296,394], which could potentially employ plasma-assisted combustion [345,347,348,395–401]. Plasma-assisted combustion strategies have been shown to decrease the lean limit of flame operation in bluff-body recirculating flame stabilizers [345,395–399], which can enable lower-emissions operation, but the level of NO emissions increases linearly with the applied discharge power [399], suggesting that the plasma power and fuel–air ratio must be optimized together to minimize emissions.

5. Summary and conclusions

Advanced biofuels derived from non-edible biomass sources, such as organic waste materials, cellulosic biomass grown with limited agricultural inputs, and algae-derived oils, can contribute to reducing energy dependence on fossil fuels and lowering greenhouse-gas emissions from transportation. Research and development of new technologies to transform the biomass into different kinds of fuels is working towards increasing energy efficiency and reducing conversion costs. The long-term trend in the industry appears to be moving away from generating an ever-increasing array of potential new fuel molecules to developing conversion technologies that produce drop-in fuels compatible with existing infrastructure and vehicles.

Current combustion engines have been optimized over a century to work with the available petroleum hydrocarbon fuels.

Advances in our understanding of the influence of specific chemical compounds on the resulting combustion performance, and attendant emissions, of a fuel enables the tailoring of a fuel, or fuel blend, for an existing engine technology or the tuning of an engine for a desired fuel. The former is much easier to accomplish with an existing legacy fleet and, thus, it appears to be the most likely route forward in the short term. The extra processing of the fuel needed to have it match an engine technology as a drop-in fuel has costs in terms of economics, energy efficiency, and life-cycle emissions that need to be considered. This is the clear trade-off in biofuel conversion and combustion technologies: the further the fuel is processed to match existing engines the lower the overall system efficiency, but this is offset in the short term by avoiding a costly overhaul of the fleet with new technology. Less refining of the raw fuels can lead to improved overall life-cycle energy efficiency, but differences in the combustion characteristics of these new fuels, and the resulting pollutant emissions, must be addressed through combustion research and advanced engine development.

The fundamental combustion and emissions properties of advanced biofuels, and their blends with petro-fuels, influence engine performance and emissions. Both oxygenated and synthetic-hydrocarbon biofuels have high-temperature combustion properties that are similar to petro-fuels, with the largest differences under the low-temperature chemistry conditions important for determining the octane and cetane numbers and the resulting performance in compression-ignition diesel and HCCI engines. Generally, oxygenated biofuels produce lower intrinsic NO_x and soot emissions than petro-fuels, mainly due to the removal of some fuel carbon from the radical pool that leads to prompt-NO and soot formation, because of the initial carbon–oxygen bonds in the oxygenated fuel. The results from specific engine tests can be affected by a host of complicating, but reasonably-well understood, factors. Synthetic hydrocarbons from biomass-to-liquid or hydrotreatment technologies are drop-in fuels with excellent compatibility with existing infrastructure and, generally, improve engine performance and reduce total emissions compared to petro-fuels, mainly due to their reduced concentration of aromatic hydrocarbon components. Combustion design tools, and a variety of fundamental laboratory combustion apparatus for validating these models, exist to analyze any potential new fuel molecule, or blend, for compatibility with existing engines, or to design a new engine or combustor for a specific fuel blend.

Advanced internal-combustion engines are aiming at improving fuel efficiency, while reducing pollutant emissions, by utilizing low-temperature combustion strategies. Current ignition and combustion control strategies appear to require tighter fuel specifications than are needed for traditional SI and CI engines. It appears that advanced diesel and HCCI engines will both require fuel properties that are more similar to each other than are traditional gasoline and diesel fuels, which will drive demand for the products of specifically-tuned and high-efficiency thermal or biochemical conversion processes. In contrast, fuel-flexible combustion or reformation coupled with external-combustion engines or fuel cells could lead to high-efficiency and ultra-low-emissions hybrid-electric powertrains for future ground transportation vehicles that may provide significantly lower well/field-to-wheel life-cycle emissions and lower operating costs.

Moving forward, a combination of approaches will be needed: beginning with drop-in fuels so as to reduce the carbon footprint of the global legacy vehicle fleet, while moving towards an eventual optimization of the entire biofuel life cycle including the devices that convert the fuel to shaft power or electrical energy. An increase in fuel-flexible technologies will enable consumers to switch to the cleanest and/or cheapest available fuel in

any given region at any given time, and can be accompanied by an overall increase in the system energy efficiency compared to today's vehicles and generators. These fuel-flexible, high-efficiency, and ultra-low-emissions technologies will be needed to meet society's transportation needs, while maintaining urban air quality, in the face of an energy- and carbon-constrained world.

Acknowledgments

References

[1] Maclean HL, Lave LB. Evaluating automobile fuel/propulsion system technologies. Prog Energy Combust Sci 2003;29:1–69.
[2] Reitz RD. Directions in internal combustion engine research. Combust Flame 2013;160(1):1–8.
[3] Agarwal AK. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Prog Energy Combust Sci 2007;33:233–71.
[4] Diesel R. The diesel oil engine. J Am Soc Nav Eng 1912;24:653–92.
[5] Grabowski MS, McCormick RL. Combustion of fat and vegetable oil derived fuels in diesel engines. Prog Energy Combust Sci 1998;24:125–64.
[6] Bergthorson JM, Kunst L, Levin DB, McVetty PBE, Smith DL, Vessey JK. Plant systems – biodiesel – an integrated approach for a highly efficient biofuel. In: 2nd ed.. Moo-Young Murray, editor. Comprehensive biotechnology, vol. 4; 2011. p. 87–99.
[7] Coniglio L, Bennadji H, Glaude PA, Herbinet O, Billaud F. Combustion chemical kinetics of biodiesel and related compounds (methyl and ethyl esters): experiments and modeling– advances and future refinements. Prog Energy Combust Sci 2013;39:340–82.
[8] Brunschwig C, Moussavou W, Blin J. Use of bioethanol for biodiesel production. Prog Energy Combust Sci 2012;38:283–301.
[9] Coniglio L, Coutinho JA, Clavier JY, Jolibert F, Jose J, Mokbel I, et al. Biodiesel via supercritical ethanolysis within a global analysis "feedstocks-conversion-engine" for a sustainable fuel alternative. Prog Energy Combust Sci 2014;43:1–35.
[10] Patzek TW. Thermodynamics of the corn-ethanol biofuel cycle. Crit Rev Plant Sci 2004;23:519–67.
[11] von Blottnitz H, Curran MA. A review of assessments conducted on bioethanol as a transportation fuel from a net energy, greenhouse gas, and environmental life cycle perspective. J Clean Prod Source 2007;15:607–19.
[12] Sims REH, Mabee W, Saddler JN, Taylor M. An overview of second generation biofuel technologies. Bioresour Technol 2010;101:1570–80.
[13] Naik SN, Goud VV, Rout PK, Dalai AK. Production of first and second generation biofuels: a comprehensive review. Renew Sustain Energy Rev 2010;14:578–97.
[14] Nigam PS, Singh A. Production of liquid biofuels from renewable resources. Prog Energy Combust Sci 2011;37:52–68.
[15] Atabani AE, Silitonga AS, Ong HC, Mahlia TMI, Masjuki HH, Badruddin IA, et al. Non-edible vegetable oils: a critical evaluation of oil extraction, fatty acid compositions, biodiesel production, characteristics, engine performance and emissions production. Renew Sustain Energy Rev 2013;18:211–45.
[16] Moser BR, Vaughn SF. Evaluation of alkyl esters from *Camelina sativa* oil as biodiesel and as blend components in ultra low-sulfur diesel fuel. Bioresour Technol 2010;101:646–53.
[17] Bernardo A, Howard-Hildige R, O'Connell A, Nichol R, Ryan J, Rice B, et al. Camelina oil as a fuel for diesel transport engines. Ind Crops Prod 2003;17:191–7.
[18] Openshaw K. A review of *Jatropha curcas*: an oil plant of unfulfilled promise. Biomass Energy 2000;19:1–15.
[19] Annarao S, Sidhu OP, Roy R, Tuli R, Khetrapal CL. Lipid profiling of developing *Jatropha curcas* L. seeds using ^{1}H NMR spectroscopy. Bioresour Technol 2008;99(18):9032–5.
[20] Silitonga AS, Masjuki HH, Mahlia TMI, Ong HC, Atabani AE, Chong WT. A global comparative review of biodiesel production from *Jatropha curcas* using different homogeneous acid and alkaline catalysts: study of physical and chemical properties. Renew Sustain Energy Rev 2013;24:514–33.
[21] Pandey VC, Singh K, Singh JS, Kumar A, Singh B, Singh RP. *Jatropha curcas*: a potential biofuel plant for sustainable environmental development. Renew Sustain Energy Rev 2012;16:2870–83.
[22] Lynd LR. Overview and evaluation of fuel ethanol from cellulosic biomass: technology, economics, the environment, and policy. Annu Rev Energy Environ 1996;21:403–65.
[23] Demirbas A. Progress and recent trends in biofuels. Prog Energy Combust Sci 2007;33:1–18.
[24] Limayem A, Ricke SC. Lignocellulosic biomass for bioethanol production: current perspectives, potential issues and future prospects. Prog Energy Combust Sci 2012;38:449–67.
[25] Menon V, Mala R. Trends in bioconversion of lignocellulose: biofuels, platform chemicals & biorefinery concept. Prog Energy Combust Sci 2012;38:522–50.
[26] Salvi BL, Subramanian KA, Panwar NL. Alternative fuels for transportation vehicles: a technical review. Renew Sustain Energy Rev 2013;25:401–19.
[27] Borgwardt RH. Transportation fuel from cellulosic biomass: a comparative assessment of ethanol and methanol options. Proc Inst Mech Eng Part A – J Power Energy 1999;213:399–407.
[28] Ptasinski KJ. Thermodynamic efficiency of biomass gasification and biofuels conversion. Biofuels Bioprod Biorefin 2008;2:239–53.
[29] Jin C, Yao MF, Liu HF, Lee CFF, Ji J. Progress in the production and application of n-butanol as a biofuel. Renew Sustain Energy Rev 2011;15:4080–106.
[30] Qureshi N, Ezeji TC. Butanol, 'a superior biofuel' production from agricultural residues (renewable biomass): recent progress in technology. Biofuels Bioprod Biorefin 2008;2:319–30.
[31] Garcia V, Pakkila J, Ojamo H, Muurinen E, Keiski RL. Challenges in biobutanol production: how to improve the efficiency? Renew Sustain Energy Rev 2011;15:964–80.
[32] Peralta-Yahya PP, Keasling JD. Advanced biofuel production in microbes. Biotechnol J 2010;5:147–62.
[33] Román-Leshkov Y, Barrett CJ, Liu ZY, Dumesic JA. Production of dimethyl-furan for liquid fuels from biomass-derived carbohydrates. Nature 2007;447:982–6.
[34] Mascal M, Nikitin EB. Direct, high-yield conversion of cellulose into biofuel. Angew Chem-Int Ed 2008;47:7924–6.
[35] Alonso DM, Bond JQ, Dumesic JA. Catalytic conversion of biomass to biofuels. Green Chem 2010;12:1493–513.
[36] Liu G, Yan B, Chen G. Technical review on jet fuel production. Renew Sustain Energy Rev 2013;25:59–70.
[37] Bezergianni S, Dimitriadis A. Comparison between different types of renewable diesel. Renew Sustain Energy Rev 2013;21:110–6.
[38] Swain PK, Das LM, Naik SN. Biomass to liquid: a prospective challenge to research and development in 21st century. Renew Sustain Energy Rev 2011;15:4917–33.
[39] Damartzis T, Zabaniotou A. Thermochemical conversion of biomass to second generation biofuels through integrated process design – a review. Renew Sustain Energy Rev 2011;15:366–78.
[40] Razzak SA, Hossain MM, Lucky RA, Bassi AS, de Lasa H. Integrated CO_2 capture, wastewater treatment and biofuel production by microalgae culturing – a review. Renew Sustain Energy Rev 2013;27:622–53.
[41] Bahadar A, Khan MB. Progress in energy from microalgae: a review. Renew Sustain Energy Rev 2013;27:128–48.
[42] Oncel SS. Microalgae for a macroenergy world. Renew Sustain Energy Rev 2013;26:241–64.
[43] Ribeiro LA, da Silva PP. Surveying techno-economic indicators of microalgae biofuel technologies. Renew Sustain Energy Rev 2013;25:89–96.
[44] Brennan L, Owende P. Biofuels from microalgae – a review of technologies for production, processing, and extractions of biofuels and co-products. Renew Sustain Energy Rev 2010;14:557–77.
[45] Pragya N, Pandey KK, Sahoo PK. A review on harvesting, oil extraction and biofuels production technologies from microalgae. Renew Sustain Energy Rev 2013;24:159–71.
[46] Zhu LD, Hiltunen E, Antila E, Zhong JJ, Yuan ZH, Wang ZM. Microalgal biofuels: flexible bioenergies for sustainable development. Renew Sustain Energy Rev 2014;30:1035–46.
[47] Suali E, Sarbatly R. Conversion of microalgae to biofuel. Renew Sustain Energy Rev 2012;16:4316–42.
[48] Robota HJ, Alger JC, Shafer L. Converting algal triglycerides to diesel and HEFA jet fuel fractions. Energy Fuels 2013;27:985–96.
[49] Graves C, Ebbesen SD, Mogensen M, Lackner KS. Sustainable hydrocarbon fuels by recycling CO_2 and H_2O with renewable or nuclear energy. Renew Sustain Energy Rev 2011;15:1–23.
[50] Budzianowski WM. Value-added carbon management technologies for low CO_2 intensive carbon-based energy vectors. Energy 2012;41(1):280–97.
[51] Budzianowski WM. Negative carbon intensity of renewable energy technologies involving biomass or carbon dioxide as inputs. Renew Sustain Energy Rev 2012;16(9):6507–21.

[52] Romero M, Steinfeld A. Concentrating solar thermal power and thermo-chemical fuels. Energy Environ Sci 2012;5(11):9234–45.

[53] Blakey S, Rye L, Wilson CW. Aviation gas turbine alternative fuels: a review. Proc Combust Inst 2011;33:2863–85.

[54] ASTM Standard D1655-13. Standard specification for aviation turbine fuels, ASTM International, West Conshohocken, PA, USA, 2013, http://dx.doi.org/10.1520/D1655-13, ⟨www.astm.org⟩.

[55] ASTM Standard D7566-13. Standard specification for aviation turbine fuel containing synthesized hydrocarbons, ASTM International, West Conshohocken, PA, USA, 2013, http://dx.doi.org/10.1520/D7566-13, ⟨www.astm.org⟩.

[56] Hileman JI, De la Rosa Blanco E, Bonnefoy PA, Carter NA. The carbon dioxide challenge facing aviation. Prog Aerosp Sci 2013;63:84–95.

[57] Han J, Elgowainy A, Cai H, Wang MQ. Life-cycle analysis of bio-based aviation fuels. Bioresour Technol 2013;150:447–56.

[58] Mata TM, Martins AA, Caetano NS. Microalgae for biodiesel production and other applications: a review. Renew Sustain Energy Rev 2010;14:217–32.

[59] Smeets EM, Faaij W, Andre PC, Lewandowski IM, Turkenburg WC. A bottom-up assessment and review of global bio-energy potentials to 2050. Prog Energy Combust Sci 2007;33:56–106.

[60] Bentsen NS, Felby C, Thorsen BJ. Agricultural residue production and potentials for energy and materials services. Prog Energy Combust Sci 2014;40:59–73.

[61] Long HL, Li XB, Wang H, Jia JD. Biomass resources and their bioenergy potential estimation: a review. Renew Sustain Energy Rev 2013;26:344–52.

[62] Menten F, Cheze B, Patouillard L, Bouvart F. A review of LCA greenhouse gas emissions results for advanced biofuels: the use of meta-regression analysis. Renew Sustain Energy Rev 2013;26:108–34.

[63] Mangoyana RB, Smith TF, Simpson R. A systems approach to evaluating sustainability of biofuel systems. Renew Sustain Energy Rev 2013;25:371–380.

[64] Shabani N, Akhatari S, Sowlati T. Value chain optimization of forest biomass for bioenergy production: a review. Renew Sustain Energy Rev 2013;23:299–311.

[65] Borrion AL, McManus MC, Hammond GP. Environmental life cycle assessment of lignocellulosic conversion to ethanol: a review. Renew Sustain Energy Rev 2012;16:4638–50.

[66] Wiloso EI, Heijungs R, de Snoo GR. LCA of second generation bioethanol: a review and some issues to be resolved for good LCA practice. Renew Sustain Energy Rev 2012;16:5295–308.

[67] Awudu I, Zhang J. Uncertainties and sustainability concepts in biofuel supply chain management: a review. Renew Sustain Energy Rev 2012;16:1359–68.

[68] Dijkman TJ, Benders RMJ. Comparison of renewable fuels based on their land use using energy densities. Renew Sustain Energy Rev 2010;14:3148–55.

[69] Markevicius A, Katinas V, Perednis E, Tamasauskiene M. Trends and sustainability criteria of the production and use of liquid biofuels. Renew Sustain Energy Rev 2010;14:3226–31.

[70] Hoefnagels R, Smeets E, Faaij A. Greenhouse gas footprints of different biofuel production systems. Renew Sustain Energy Rev 2010;14:1661–94.

[71] Gonzalez-Garcia S, Moreira MT, Feijoo G. Comparative environmental performance of lignocellulosic ethanol from different feedstocks. Renew Sustain Energy Rev 2010;14:2077–85.

[72] Escobar JC, Lora ES, Venturini OJ, Yanez EE, Castillo EF, Almazan O. Biofuels: environment, technology and food security. Renew Sustain Energy Rev 2009;13:1275–87.

[73] Knothe G. Biodiesel and renewable diesel: a comparison. Prog Energy Combust Sci 2010;36:364–73.

[74] Luo J, Fang Z, Smith Jr RL. Ultrasound-enhanced conversion of biomass to biofuels. Prog Energy Combust Sci 2014;41:56–93. http://dx.doi.org/10.1016/j.pecs.2013.11.001.

[75] Zhu JY, Zhuang XS. Conceptual net energy output for biofuel production from lignocellulosic biomass through biorefining. Prog Energy Combust Sci 2012;38:583–98.

[76] Larson ED. A review of life-cycle analysis studies on liquid biofuel systems for the transport sector. Energy Sustain Dev 2006;10:109–26.

[77] Shonnard DR, Williams L, Kalnes TN. Camelina-derived jet fuel and diesel: sustainable advanced biofuels. Environ Prog Sustain Energy 2010;29:382–92.

[78] Van der Giesen C, Kleijn R, Kramer GJ. Energy and climate impacts of producing synthetic hydrocarbon fuels from CO_2. Environ Sci Technol 2014;48:7111–21.

[79] Lemoine DM, Plevin RJ, Cohn AS, Jones AD, Brandt AR, Vergara SE, Kammen DM. The climate impacts of bioenergy systems depend on market and regulatory policy contexts. Environ Sci Technol 2010;44(19):7347–50.

[80] Piriou B, Vaitilingom G, Veyssiere B, Cuq B, Rouau X. Potential direct use of solid biomass in internal combustion engines. Prog Energy Combust Sci 2013;39:169–88.

[81] Watson GM, Munzar JD, Bergthorson JM. NO formation in model syngas and biogas blends. Fuel 2014;124:113–24. http://dx.doi.org/10.1016/j.fuel.2014.01.079.

[82] Cann AF, Liao JC. Pentanol isomer synthesis in engineered microorganisms. Appl Microbiol Biotechnol 2010;85(4):893–9.

[83] Koffas MA. Expanding the repertoire of biofuel alternatives through meta-bolic pathway evolution. Proc Natl Acad Sci 2009;106:965–6.

[84] Dekishima Y, Lan EI, Shen CR, Cho KM, Liao JC. Extending carbon chain length of 1-butanol pathway for 1-hexanol synthesis from glucose by engineered *Escherichia coli*. J Am Chem Soc 2011;133:11399–401.

[85] Tran LS, Sirjean B, Glaude PA, Fournet R, Battin-Leclerc F. Progress in detailed kinetic modeling of the combustion of oxygenated components of biofuels. Energy 2012;43:4–18.

[86] Kohse-Höinghaus K, Oßwald P, Cool TA, Kasper T, Hansen N, Qi F, et al. Biofuel combustion chemistry: from ethanol to biodiesel. Angew Chem-Int Ed 2010;49:3572–97.

[87] Westbrook CK. Biofuels Combustion. Annu Rev Phys Chem 2013;64:201–19.

[88] Metzger P, Largeau C. *Botryococcus braunii*: a rich source for hydrocarbons and related ether lipids. Appl Microbiol Biotechnol 2005;66:486–96.

[89] Hu Q, Sommerfeld M, Jarvis E, Ghirardi M, Posewitz M, Seibert M, Darzins A. Microalgal triacylglycerols as feedstocks for biofuel production: perspectives and advances. Plant J 2008;54(4):621–39.

[90] Dunn RO. Effects of minor constituents on cold flow properties and performance of biodiesel. Prog Energy Combust Sci 2009;35:481–9.

[91] Probstein RF, Hicks RE. Synthetic fuels. Mineola, New York: Dover Publications Inc.; 2006.

[92] Dry ME. The Fischer–Tropsch process: 1950–2000. Catal Today 2002;71:227–41.

[93] Dry ME. High quality diesel via the Fischer–Tropsch process – a review. J Chem Technol Biotechnol 2002;77:43–50.

[94] Gill SS, Tsolakis A, Dearn KD, Rodríguez-Fernández J. Combustion characteristics and emissions of Fischer–Tropsch diesel fuels in IC engines. Prog Energy Combust Sci 2011;37:503–23.

[95] Corporan E, Edwards I, Shafer L, DeWitt MJ, Klinghsirn C, Zabarnick S, et al. Chemical, thermal stability, seal swell, and emissions studies of alternative jet fuels. Energy Fuels 2011;25:955–66.

[96] Graham JL, Striebich RC, Myers KJ, Minus DK, Harrison III WE. Swelling of nitrile rubber by selected aromatics blended in a synthetic jet fuel. Energy Fuels 2006;20:759–65.

[97] Di Blasi C. Modeling chemical and physical processes of wood and biomass pyrolysis. Prog Energy Combust Sci 2008;34:47–90.

[98] Bridgwater AV. Renewable fuels and chemicals by thermal processing of biomass. Chem Eng J 2003;91:87–102.

[99] Czernik S, Bridgwater AV. Overview of applications of biomass fast pyrolysis oil. Energy Fuels 2004;18:590–8.

[100] Tzanetakis T, Moloodi S, Farra N, Nguyen B, McGrath A, Thomson M. Comparison of the spray combustion characteristics and emissions of a wood-derived fast pyrolysis liquid-ethanol blend with number 2 and number 4 fuel oils in a pilot-stabilized swirl burner. Energy Fuels 2011;25(10):4305–21.

[101] Hossain AK, Davies PA. Pyrolysis liquids and gases as alternative fuels in internal combustion engines – a review. Renew Sustain Energy Rev 2013;21:165–89.

[102] Butler E, Devlin G, Meier D, McDonnell K. A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading. Renew Sustain Energy Rev 2011;15:4171–86.

[103] Jacobson K, Maheria KC, Dalai AK. Bio-oil valorization: a review. Renew Sustain Energy Rev 2013;23:91–106.

[104] United-States-Environmental-Protection-Agency. Nitrogen dioxide – health. Available: ⟨http://www.epa.gov/airquality/nitrogenoxides/health.html⟩ [02.08.14].

[105] Bowman CT. Kinetics of pollutant formation and destruction in combustion. Prog Energy Combust Sci 1975;1:33–45.

[106] Miller JA, Bowman CT. Mechanism and modeling of nitrogen chemistry in combustion. Prog Energy Combust Sci 1989;15:287–338.

[107] Beér JM. Combustion technology developments in power generation in response to environmental challenges. Prog Energy Combust Sci 2000;26(4):301–27.

[108] United-States-Environmental-Protection-Agency. Particulate matter – health. Available: ⟨http://www.epa.gov/airquality/particlepollution/health.html⟩ [02.08.14].

[109] Haynes BS, Wagner HG. Soot formation. Prog Energy Combust Sci 1981;7(4):229–73.

[110] Tree DR, Svensson KI. Soot processes in compression ignition engines. Prog Energy Combust Sci 2007;33:272–309.

[111] United-States-Environmental-Protection-Agency. Ground level ozone – basic information. Available: ⟨http://www.epa.gov/airquality/ozonepollution/basic.html⟩ [02.08.14].

[112] Alkidas AC. Combustion-chamber crevices: the major source of engine-out hydrocarbon emissions under fully warmed conditions. Prog Energy Combust Sci 1999;25:253–73.

[113] Graham LA, Belisle SL, Baas CL. Emissions from light duty gasoline vehicles operating on low blend ethanol gasoline and E85. Atmos Environ 2008;42:4498–516.

[114] United-States-Environmental-Protection-Agency. Carbon monoxide – health. Available: ⟨http://www.epa.gov/airquality/carbonmonoxide/health.html⟩ [02.08.14].

[115] United-States-Environmental-Protection-Agency. Ground level ozone – health. Available: ⟨http://www.epa.gov/airquality/ozonepollution/health.html⟩ [02.08.14].

[116] United-States-Environmental-Protection-Agency. Effects of acid rain. Available: ⟨http://www.epa.gov/acidrain/effects/index.html⟩ [02.08.14].

[117] United-States-Environmental-Protection-Agency. Effects of acid rain – surface waters and aquatic animals. Available: ⟨http://www.epa.gov/acidrain/effects/surface_water.html⟩ [02.08.14].

[118] United-States-Environmental-Protection-Agency. Effects of acid rain – forests. Available: ⟨http://www.epa.gov/acidrain/effects/forests.html⟩ [02.08.14].

[119] United-States-Environmental-Protection-Agency. Sulfur dioxide – health. Available: ⟨http://www.epa.gov/airquality/sulfurdioxide/health.html⟩ [02.08.14].

[120] United-States-Environmental-Protection-Agency. Acid rain. Available: ⟨http://www.epa.gov/acidrain/index.html⟩ [02.08.14].

[121] McIlroy A, McRae G, Sick V, Siebers DL, Westbrook CK, Smith PJ, et al. Basic research needs for clean and efficient combustion of 21st century transportation fuels. US Department of Energy Report. ⟨http://www.osti.gov/scitech/biblio/935428⟩; 2006 [accessed 12.02.13] ⟨http://dx.doi.org/10.2172/935428⟩.

[122] Zhao F, Lai MC, Harrington DL. Automotive spark-ignited direct-injection gasoline engines. Prog Energy Combust Sci 1999;25(5):437–562.

[123] Yao M, Zheng Z, Liu H. Progress and recent trends in homogeneous charge compression ignition (HCCI) engines. Prog Energy Combust Sci 2009;35: 398–437.

[124] Alkidas AC. Combustion advancements in gasoline engines. Energy Convers Manag 2007;48(11):2751–61.

[125] Myung CL, Park S. Exhaust nanoparticle emissions from internal combustion engines: a review. Int J Automot Technol 2012;13(1):9–22.

[126] Westbrook CK. Chemical kinetics of hydrocarbon ignition in practical combustion systems. Proc Combust Inst 2000;28:1563–77.

[127] Robert A, Richard S, Colin O, Martinez L, de Franqueville L. LES prediction and analysis of knocking combustion in a spark ignition engine. Proc Combust Inst 2014. http://dx.doi.org/10.1016/j.proci.2014.05.154 (in press).

[128] Driscoll JF. Turbulent premixed combustion: flamelet structure and its effect on turbulent burning velocities. Prog Energy Combust Sci 2008;34 (1):91–134.

[129] Chaudhuri S, Wu F, Zhu D, Law CK. Flame speed and self-similar propagation of expanding turbulent premixed flames. Phys Rev Lett 2012;108(4):044503.

[130] ASTM Standard D4814-13b. Standard specification for automotive spark-ignition engine fuel, ASTM International, West Conshohocken, PA, USA, 2013, http://dx.doi.org/10/1520/D4814-13. ⟨www.astm.org⟩.

[131] Westbrook CK, Mizobuchi Y, Poinsot TJ, Smith PJ, Warnatz E. Computational combustion. Proc Combust Inst 2005;30:125–57.

[132] Battin-Leclerc F. Detailed chemical kinetic models for the low-temperature combustion of hydrocarbons with application to gasoline and diesel fuel surrogates. Prog Energy Combust Sci 2008;34:440–98.

[133] Zador J, Taatjes CA, Fernandes RX. Kinetics of elementary reactions in low-temperature auto-ignition chemistry. Prog Energy Combust Sci 2011;37:371–421.

[134] Litzinger TA. A review of experimental studies of knock chemistry in engines. Prog Energy Combust Sci 1990;16(3):155–67.

[135] Lignola PG, Reverchon E. Cool flames. Prog Energy Combust Sci 1987;13 (1):75–96.

[136] Blurock E, Battin-Leclerc F. Modeling combustion with detailed kinetic mechanisms. In: Battin-Leclerc F, Simmie JM, Blurock. E, editors. Cleaner combustion. London: Springer; 2013. p. 17–57.

[137] Griffiths JF, Scott SK. Thermokinetic interactions: fundamentals of spontaneous ignition and cool flames. Prog Energy Combust Sci 1987;13(3):161–97.

[138] Chaos M, Kazakov A, Zhao Z, Dryer FL. A high-temperature chemical kinetic model for primary reference fuels. Int J Chem Kinet 2007;39(7):399–414.

[139] Morgan N, Smallbone A, Bhave A, Kraft M, Cracknell R, Kalghatgi G. Mapping surrogate gasoline compositions into RON/MON space. Combust Flame 2010;157(6):1122–31.

[140] Foong TM, Morganti KJ, Brear MJ, da Silva G, Yang Y, Dryer FL. The octane numbers of ethanol blended with gasoline and its surrogates. Fuel 2014;115:727–39.

[141] Knop V, Loos M, Pera C, Jeuland N. A linear-by-mole blending rule for octane numbers of n-heptane/iso-octane/toluene mixtures. Fuel 2014;115:666–73.

[142] Haas FM, Dryer FL. Application of blending rules for ignition quality metrics: a comment on "A linear-by-mole blending rule for octane numbers of n-heptane/iso-octane/toluene mixtures". Fuel 2014;120:240–2.

[143] Westbrook CK, Dryer FL. Chemical kinetic modeling of hydrocarbon combustion. Prog Energy Combust Sci 1984;10(1):1–57.

[144] Mehl M, Pitz WJ, Westbrook CK, Curran HJ. Kinetic modeling of gasoline surrogate components and mixtures under engine conditions. Proc Combust Inst 2011;33:193–200.

[145] Law CK. Fuel options for next-generation chemical propulsion. AIAA J 2012;50:19–36.

[146] Schofield K. Large scale chemical kinetic models of fossil fuel combustion: adequate as engineering models – no more, no less. Energy Fuels 2012;26:5468–80.

[147] Miller JA, Kee RJ, Westbrook CK. Chemical kinetics and combustion modeling. Ann Rev Phys Chem 1990;41:345–87.

[148] Ranzi E, Frassoldati A, Grana R, Cuoci A, Faravelli T, Kelley AP, et al. Hierarchical and comparative kinetic modeling of laminar flame speeds of hydrocarbon and oxygenated fuels. Prog Energy Combust Sci 2012;38: 468–501.

[149] Warnatz J. Chemistry of high temperature combustion of alkanes up to octane. Proc Combust Inst 1984;20:845–56.

[150] Dooley S, Won SH, Heyne J, Farouk TI, Ju YG, Dryer FL, et al. The experimental evaluation of a methodology for surrogate fuel formulation to emulate gas phase combustion kinetic phenomena. Combust Flame 2012;159:1444–66.

[151] Schofield K, Steinberg M. CH and C_2 measurements imply a radical pool within a pool in acetylene flames. J Phys Chem A 2007;111(11):2098–114.

[152] Lu T, Law CK. Toward accommodating realistic fuel chemistry in large-scale computations. Prog Energy Combust Sci 2009;35:192–215.

[153] Akih-Kumgeh B, Bergthorson JM. Skeletal chemical kinetic mechanisms for syngas, methyl butanoate, n-heptane and n-decane. Energy Fuels 2013;27:2316–26.

[154] Tomlin AS, Turányi T. Mechanism reduction to skeletal form and species lumping. In: Battin-Leclerc F, Simmie JM, Blurock E, editors. Cleaner combustion. London: Springer; 2013. p. 447–66.

[155] Ranzi E, Frassoldati A, Stagni A, Pelucchi M, Cuoci A, Faravelli T. Reduced kinetic schemes of complex reaction systems: fossil and biomass-derived transportation fuels. Int J Chem Kinet 2014;46(9):512–42.

[156] Munzar JD, Akih-Kumgeh B, Denman BM, Zia A, Bergthorson JM. An experimental and reduced modeling study of the laminar flame speed of jet fuel surrogate components. Fuel 2013;113:586–97.

[157] Akih-Kumgeh B, Bergthorson JM. A four component skeletal model for the analysis of jet fuel surrogate combustion. In: Proceedings of the ASME Turbo Expo 2013. ASME paper GT2013-94813. San Antonio, Texas; 2013. http://dx.doi.org/10.1115/GT2013-94813.

[158] Misdariis A, Vermorel O, Poinsot T. A methodology based on reduced schemes to compute auto-ignition and propagation in internal combustion engines. Proc Combust Inst 2014. http://dx.doi.org/10.1016/j.proci.2014.06.053 (in press).

[159] Gautam M, Martin II DW. Combustion characteristics of higher-alcohol/gasoline blends. Proc Inst Mech Eng Part A – J Power Energy 2000;214: 497–511.

[160] ASTM Standard D4806-13a. Standard specification for denatured fuel ethanol for blending with gasolines for use as automotive spark-ignition engine fuel, ASTM International, West Conshohocken, PA, USA, 2013, http://dx.doi.org/10.1520/D4806-13, ⟨www.astm.org⟩.

[161] ASTM Standard D5798-13a. Standard specification for ethanol fuel blends for flexible-fuel automotive spark-ignition engines, ASTM International, West Conshohocken, PA, USA, 2013, http://dx.doi.org/10.1520/D5798-13, ⟨www.astm.org⟩.

[162] ASTM Standard D5797-13. Standard specification for fuel methanol (M70-M85) for automotive spark-ignition engines, ASTM International, West Conshohocken, PA, USA, 2013, http://dx.doi.org/10.1520/D5797-13, ⟨www.astm.org⟩.

[163] Carrette L, Friedrich KA, Stimming U. Fuel cells: principles, types, fuels, and applications. ChemPhysChem 2000;1:162–93.

[164] Palo DR, Dagle RA, Holladay JD. Methanol steam reforming for hydrogen production. Chem Rev 2007;107:3992–4021.

[165] Pan C, He RH, Li QF, Jensen JO, Bjerrum NJ, Hjulmand HA, Jensen AB. Integration of high temperature PEM fuel cells with a methanol reformer. J Power Sources 2005;145(2):392–8.

[166] Kee RJ, Zhu H, Goodwin DG. Solid-oxide fuel cells with hydrocarbon fuels. Proc Combust Inst 2005;30:2379–404.

[167] Moss JT, Berkowitz AM, Oehlschlaeger MA, Biet J, Warth V, Glaude PA, et al. An experimental and kinetic modeling study of the oxidation of the four isomers of butanol. J Phys Chem A 2008;112:10843–55.

[168] ASTM Standard D7862-13. Standard specification for butanol for blending with gasoline for use as automotive spark-ignition engine fuel, ASTM International, West Conshohocken, PA, USA, 2013, http://dx.doi.org/10.1520/D7862-13, ⟨www.astm.org⟩.

[169] Haas FM, Chaos M, Dryer FL. Low and intermediate temperature oxidation of ethanol and ethanol-PRF blends: an experimental and modeling study. Combust Flame 2009;156:2346–50.

[170] Saxena S, Bedoya ID. Fundamental phenomena affecting low temperature combustion and HCCI engines, high load limits and strategies for extending these limits. Prog Energy Combust Sci 2013;39:457–88.

[171] Karwat DMA, Wagnon SW, Wooldridge MS, Westbrook CK. On the combustion chemistry of n-heptane and n-butanol blends. J Phys Chem A 2012;116:12406–21.

[172] Zhang J, Niu S, Zhang Y, Tang C, Jiang X, Hu E, et al. Experimental and modeling study of the auto-ignition of n-heptane/n-butanol mixtures. Combust Flame 2013;160:31–9.

[173] Heufer KA, Bugler J, Curran HJ. A comparison of longer alkane and alcohol ignition including new experimental results for n-pentanol and n-hexanol. Proc Combust Inst 2013;34:511–8.

[174] Heufer KA, Sarathy SM, Curran HJ, Davis AC, Westbrook CK, Pitz WJ. Detailed kinetic modeling study of n-pentanol oxidation. Energy Fuels 2012;26: 6678–85.

[175] Cai L, Uygun Y, Togbé C, Pitsch H, Olivier H, Dagaut P, et al. An experimental and modeling study of n-octanol combustion. Proc Combust Inst 2014. http://dx.doi.org/10.1016/j.proci.2014.05.088 (in press).

[176] Haas FM, Ramcharan A, Dryer FL. Relative reactivities of the isomeric butanols and ethanol in an ignition quality tester. Energy Fuels 2011;25: 3909–16.

[177] Sileghem L, Alekseev VA, Vancoillie J, Van Geem KM, Nilsson EJK, Verhelst S, et al. Laminar burning velocity of gasoline and the gasoline surrogate components iso-octane, n-heptane and toluene. Fuel 2013;112:355–65.

[178] Ji C, Sarathy SM, Veloo PS, Westbrook CK, Egolfopoulos FN. Effects of fuel branching on the propagation of octane isomers flames. Combust Flame 2012;159:1426–36.

[179] Mehl M, Herbinet O, Dirrenberger P, Bounaceur R, Glaude PA, Battin-Leclerc F, et al. Experimental and modeling study of burning velocities for alkyl

aromatic components relevant to diesel fuels. Proc Combust Inst 2014. http://dx.doi.org/10.1016/j.proci.2014.06.064 (in press).

[180] Veloo PS, Wang YL, Egolfopoulos FN, Westbrook CK. A comparative experimental and computational study of methanol, ethanol, and *n*-butanol flames. Combust Flame 2010;157:1989–2004.

[181] Broustail G, Halter F, Seers P, Moreac G, Mounaim-Rousselle C. Experimental determination of laminar burning velocity for butanol/*iso*-octane and ethanol/*iso*-octane blends for different initial pressures. Fuel 2013;106:310–7.

[182] Li Q, Hu E, Cheng Y, Huang Z. Measurements of laminar flame speeds and flame instability analysis of 2-methyl-1-butanol–air mixtures. Fuel 2013;112:263–71.

[183] van Lipzig JPJ, Nilsson EJK, de Goey LPH, Konnov AA. Laminar burning velocities of *n*-heptane, *iso*-octane, ethanol and their binary and tertiary mixtures. Fuel 2011;90:2773–81.

[184] Varea E, Modica V, Renou B, Boukhalfa AM. Pressure effects on laminar burning velocities and Markstein lengths for isooctane–ethanol–air mixtures. Proc Combust Inst 2013;34:735–44.

[185] Zhang X, Tang C, Yu H, Li Q, Gong J, Huang Z. Laminar flame characteristics of *iso*-octane/*n*-butanol blend–air mixtures at elevated temperatures. Energy Fuels 2013;27:2327–35.

[186] Wu F, Law CK. An experimental and mechanistic study on the laminar flame speed, Markstein length and flame chemistry of the butanol isomers. Combust Flame 2013;160:2744–56.

[187] Li Q, Hu E, Zhang X, Cheng Y, Huang Z. Laminar flame speeds and flame instabilities of pentanol isomer–air mixtures at elevated temperatures and pressures. Energy Fuels 2013;27:1141–50.

[188] Noorani KE, Akih-Kumgeh B, Bergthorson JM. Comparative high temperature shock tube ignition of C1–C4 primary alcohols. Energy Fuels 2010;24:5834–43.

[189] Tang C, Wei L, Man X, Zhang J, Huang Z, Law CK. High temperature ignition delay times of C5 primary alcohols. Combust Flame 2013;160:520–9.

[190] Johnson MV, Goldsborough SS, Serinyel Z, O'Toole P, Larkin E, O'Malley G, et al. A shock tube study of n-and iso-propanol ignition. Energy Fuels 2009;23(12):5886–98.

[191] Ihracska B, Korakianitis T, Ruiz P, Emberson DR, Crookes RJ, Diez A, et al. Assessment of elliptic flame front propagation characteristics of *iso*-octane, gasoline, M85 and E85 in an optical engine. Combust Flame 2014;161:696–710.

[192] Aleiferis PG, Serras-Pereira J, Richardson D. Characteristic of flame development with ethanol, butanol, *iso*-octane, gasoline and methane in a direct-injection spark-ignition engine. Fuel 2013;109:256–78.

[193] Wu F, Saha A, Chaudhuri S, Law CK. Propagation speeds of expanding turbulent flames of C4 to C8 n-alkanes at elevated pressures: experimental determination, fuel similarity, and stretch-affected local extinction. Proc Combust Inst 2014. http://dx.doi.org/10.1016/j.proci.2014.07.070 (in press).

[194] Marinov NM. A detailed chemical kinetic model for high temperature ethanol oxidation. Int J Chem Kinet 1999;31:183–220.

[195] Sarathy SM, Thomson MJ, Togbe C, Dagaut P, Halter F, Mounaim-Rousselle C. An experimental and kinetic modeling study of *n*-butanol combustion. Combust Flame 2008;156:852–64.

[196] Black G, Curran HJ, Pichon S, Simmie JM, Zhukov V. Bio-butanol: combustion properties and detailed chemical kinetic model. Combust Flame 2010;157:363–73.

[197] Vasu SS, Sarathy SM. On the high-temperature combustion of *n*-butanol: shock tube data and an improved kinetic model. Energy Fuels 2013;27:7072–80.

[198] Sarathy SM, Park S, Weber BW, Wang W, Veloo PS, Davis AC, et al. A comprehensive experimental and modeling study of *iso*-pentanol combustion. Combust Flame 2013;160:2712–28.

[199] Togbe C, Dagaut P, Mzé-Ahmed A, Diévart P, Halter F, Foucher F. Experimental and detailed kinetic modeling study of 1-hexanol oxidation in a pressurized jet-stirred reactor and a combustion bomb. Energy Fuels 2010;24:5859–75.

[200] Yeung C, Thomson MJ. Experimental and kinetic modeling study of 1-hexanol combustion in an opposed-flow diffusion flame. Proc Combust Inst 2013;34:795–802.

[201] Sarathy SM, Oßwald P, Hansen N, Kohse-Höinghaus K. Alcohol combustion chemistry. Prog Energy Combust Sci 2014;44:40–102.

[202] Karavalakis G, Short D, Vu D, Villela M, Asa-Awuku A, Durbin TD. Evaluating the regulated emissions, air toxics, ultrafine particles, and black carbon from SI-PFI and SI-DI vehicles operating on different ethanol and iso-butanol blends. Fuel 2014;128:410–21.

[203] Canakci M, Ozsezen AN, Alptekin E, Eyidogan M. Impact of alcohol–gasoline fuel blends on the exhaust emission of an SI engine. Renew Energy 2013;52:111–7.

[204] Gravalos I, Moshou D, Gialamas T, Xyradakis P, Kateris D, Tsiropoulos Z. Emissions characteristics of spark ignition engine operating on lower–higher molecular mass alcohol blended gasoline fuels. Renew Energy 2013;50:27–32.

[205] Balki MK, Sayin C, Canakci M. The effect of different alcohol fuels on the performance, emission and combustion characteristics of a gasoline engine. Fuel 2014;115:901–6.

[206] Hill SC, Smoot LD. Modeling of nitrogen oxides formation and destruction in combustion systems. Prog Energy Combust Sci 2000;26:417–58.

[207] Watson GMG, Munzar JD, Bergthorson JM. Experimental diagnostics and modelling of jet–wall stagnation flames for NO_x sub-model validation. Energy Fuels 2013;27(11):7031–43.

[208] Watson GMG, Versailles P, Bergthorson JM. NO formation in premixed flames of C1 to C3 alkanes and alcohols. Combust Flame 2014 (in preparation).

[209] Li SC, Williams FA. Formation of NO_x, CH_4, and C_2 species in laminar methanol flames. Proc Combust Inst 1998;27:485–93.

[210] Saxena P, Williams FA. Numerical and experimental studies of ethanol flames. Proc Combust Inst 2007;31:1149–56.

[211] Chung GA, Akih-Kumgeh B, Watson GMG, Bergthorson JM. NO_x formation and flame velocity profiles of *iso*- and *n*-isomers of butane and butanol. Proc Combust Inst 2013;34:831–8.

[212] Watson GMG, Versailles P, Bergthorson JM. NO formation in premixed flames of C_4 alkanes and alcohols. Combust Flame 2014 (in preparation).

[213] Sutton JA, Williams BA, Fleming JW. Investigation of NCN and prompt-NO formation in low-pressure C1–C4 alkane flames. Combust Flame 2012;159:562–76.

[214] Versailles P, GMG Watson, Lipardi A, Bergthorson JM. Quantitative CH measurements in atmospheric-pressure, premixed flames of C_1–C_4 alkanes. Combustion and Flame 2014 (in preparation).

[215] Zsély IG, Zádor J, Turányi T. Uncertainty analysis of NO production during methane combustion. Int J Chem Kinet 2008;40(11):754–68.

[216] Wei LJ, Tang CL, Man XJ, Jiang X, Huang ZH. High-temperature ignition delay times and kinetic study of furan. Energy Fuels 2012;26:2075–81.

[217] Tian ZY, Yuan T, Fournet R, Glaude PA, Sirjean B, Battin-Leclerc F, et al. An experimental and kinetic investigation of premixed furan/oxygen/argon flames. Combust Flame 2011;158:756–73.

[218] Somers KP, Simmie JM, Gillespie F, Burke U, Connolly J, Metcalfe WK, et al. A high temperature and atmospheric pressure experimental and detailed chemical kinetic modeling study of 2-methyl furan oxidation. Proc Combust Inst 2013;34:225–32.

[219] Nilsson EJ, Konnov AA. Flame studies of oxygenates. In: Battin-Leclerc F, Simmie E, Blurock E, editors. Cleaner combustion. London: Springer; 2013. p. 231–80.

[220] Sudholt A, Cai L, Heyne J, Haas FM, Pitsch H, Dryer FL. Ignition characteristics of a bio-derived class of saturated and unsaturated furans for engine applications. Proc Combust Inst 2014. http://dx.doi.org/10.1016/j.proci.2014.06.147 (in press).

[221] Eldeeb MA, Akih-Kumgeh B. Reactivity Trends in Furan and Alkyl Furan Combustion. Energy Fuels 2014;28(10):6618–26. http://dx.doi.org/10.1021/ef501181z (in press).

[222] Tran LS, Sirjean B, Glaude PA, Kohse-Höinghaus K, Battin-Leclerc F. Influence of substituted furans on the formation of Polycyclic Aromatic Hydrocarbons in flames. Proc Combust Inst 2014. http://dx.doi.org/10.1016/j.proci.2014.06.137 (in press).

[223] Sarathy SM, Kukkadapu G, Mehl M, Wang W, Javed T, Park S, et al. Ignition of alkane-rich FACE gasoline fuels and their surrogate mixtures. Proc Combust Inst 2014. http://dx.doi.org/10.1016/j.proci.2014.05.122 (in press).

[224] Caprino L, Togna GI. Potential health effects of gasoline and its constituents: a review of current literature (1990–1997) on toxicological data. Environ Health Perspect 1998;106:115–25.

[225] Ahmed FE. Toxicology and human health effects following exposure to oxygenated or reformulated gasoline. Toxicol Lett 2001;123:89–113.

[226] McGregor D. Methyl tertiary-butyl ether: studies for potential human health hazards. Crit Rev Toxicol 2006;36:319–58.

[227] Phillips S, Palmer RB, Brody A. Epidemiology, toxicokinetics, and health effects of methyl tert-butyl ether (MTBE). J Med Toxicol 2008;4:115–26.

[228] Cowden N, Prinzinger J, Prinzinger M. A public choice model of environmental legislation: MTBE vs. ethanol. Oxf J 2009;8:223–31.

[229] Dec JE. Advanced compression-ignition engines – understanding the in-cylinder processes. Proc Combust Inst 2009;32(2):2727–42.

[230] Ronney PD, Shoda M, Waida ST, Durbin EJ. Throttleless premixed-charge engines: concept and experiment. Proc Inst Mech Eng Part D: J Automob Eng 1994;208(1):13–24. http://dx.doi.org/10.1243/PIME_PROC_1994_208_153_02.

[231] Alagumalai A. Internal combustion engines: progress and prospects. Renew Sustain Energy Rev 2014;38:561–71.

[232] Sweeney MS, Hochgreb S, Barlow RS. The structure of premixed and stratified low turbulence flames. Combust Flame 2011;158(5):935–48.

[233] Dec JE. A conceptual model of DI diesel combustion based on laser-sheet imaging. SAE Technical Paper 970873; 1997, http://dx.doi.org/10.4271/970873.

[234] Weinberg FJ. The first half-million years of combustion research and today's burning problems. Prog Energy Combust Sci 1975;1(1):17–31.

[235] ASTM Standard D975-13a. Standard specification for diesel fuel oils, ASTM International, West Conshohocken, PA, USA, 2013, http://dx.doi.org/10.1520/D975-13, ⟨www.astm.org⟩.

[236] Pitz WJ, Mueller CJ. Recent progress in the development of diesel surrogate fuels. Prog Energy Combust Sci 2011;37:330–50.

[237] Musculus MPB, Miles PC, Pickett LM. Conceptual models for partially premixed low-temperature diesel combustion. Prog Energy Combust Sci 2013;39:246–83.

[238] Westbrook CK, Pitz WJ, Curran HJ. Chemical kinetic modeling study of the effects of oxygenated hydrocarbons on soot emissions from diesel engines. J Phys Chem A 2006;110:6912–22.

[239] Westbrook CK, Pitz WJ, Herbinet O, Curran HJ, Silke EJ. A comprehensive detailed chemical kinetic reaction mechanism for combustion of *n*-alkane

hydrocarbons from *n*-octane to *n*-hexadecane. Combust Flame 2009;156: 181–99.

[240] Westbrook CK, Pitz WJ, Mehl M, Curran HJ. Detailed chemical kinetic reaction mechanisms for primary reference fuels for diesel cetane number and spark-ignition octane number. Proc Combust Inst 2011;33:185–92.

[241] Westbrook CK, Pitz WJ, Sarathy SM, Mehl M. Detailed chemical kinetic modeling of the effects of C=C double bonds on the ignition of biodiesel fuels. Proc Combust Inst 2013;34:3049–56.

[242] Lai JYW, Lin KC, Violi A. Biodiesel combustion: advances in chemical kinetic modeling. Prog Energy Combust Sci 2011;37:1–14.

[243] Lapuerta M, Armas O, Rodriguez-Fernandez J. Effect of biodiesel fuels on diesel engine emissions. Prog Energy Combust Sci 2008;34:198–223.

[244] Sun J, Caton JA, Jacobs TJ. Oxides of nitrogen emissions from biodiesel fueled diesel engines. Prog Energy Combust Sci 2010;26:667–95.

[245] Giakoumis EG, Rakopoulos CD, Dimaratos AM, Rakopoulos DC. Exhaust emissions of diesel engines operating under transient conditions with biodiesel fuel blends. Prog Energy Combust Sci 2012;38:691–715.

[246] Palash SM, Kalam MA, Masjuki HH, Masum BM, Rizwanul Fattah IM, Mofijur M. Impacts of biodiesel combustion on NO_x emissions and their reduction approaches. Renew Sustain Energy Rev 2013;23:473–90.

[247] Xue J, Grift TE, Hansen AC. Effect of biodiesel on engine performances and emissions. Renew Sustain Energy Rev 2011;15:1098–116.

[248] Varatharajan K, Cheralathan M. Influence of fuel properties and composition on NO_x emissions from biodiesel powered diesel engines: a review. Renew Sustain Energy Rev 2012;16:3702–10.

[249] Szybist JP, Song J, Alam M, Boehman AL. Biodiesel combustion, emissions and emission control. Fuel Process Technol 2007;88:679–91.

[250] Hoekman SK, Robbins C. Review of the effects of biodiesel on NO_x emissions. Fuel Process Technol 2012;96:237–49.

[251] Mueller CJ, Boehman AL, Martin GC. An experimental investigation of the origin of increased NO_x emissions when fueling a heavy-duty compression-ignition engine with soy biodiesel. SAE Paper 2009-01-1792.

[252] Szybist JP, Kearby SR, Boehman AL. NO_x emissions of alternative diesel fuels: a comparative analysis of biodiesel and FT diesel. Energy Fuels 2005;19:1484–92.

[253] Rajasekar E, Murugesan A, Subramanian R, Nedunchezhian N. Review of NO_x reduction technologies in CI engines fuelled with oxygenated biomass fuels. Renew Sustain Energy Rev 2010;14:2113–21.

[254] ASTM Standard D7467-13. Standard specification for diesel fuel oil, biodiesel blend (B6 to B20), ASTM International, West Conshohocken, PA, USA, 2013, http://dx.doi.org/10.1520/D7467-13, ⟨www.astm.org⟩.

[255] ASTM Standard D6751-12. Standard specification for biodiesel fuel blend stock (B100) for middle distillate fuels, ASTM International, West Conshohocken, PA, USA, 2012, http://dx.doi.org/10.1520/D6751-12, ⟨www.astm.org⟩.

[256] European Standard EN590:2013. Automotive fuels – diesel – requirements and test methods. Brussels, Belgium: European Committee for Standardization; 2013.

[257] European Standard EN14214:2012. Liquid petroleum products – fatty acid methyl esters (FAME) for use in diesel engines and heating applications – requirements and test methods. Brussels, Belgium: European Committee for Standardization; 2013.

[258] Wang W, Gowdagiri S, Oehlschlaeger MA. Comparative study of the auto-ignition of methyl decenoates, unsaturated biodiesel fuel surrogates. Energy Fuels 2013;27:5527–32.

[259] Akih-Kumgeh B, Bergthorson JM. Structure-reactivity trends of C1–C4 alkanoic acid methyl esters. Combust Flame 2011;158:1037–48.

[260] Akih-Kumgeh B, Bergthorson JM. Comparative study of methyl butanoate and *n*-heptane high temperature auto-ignition. Energy Fuels 2010;24: 2439–48.

[261] Wang W, Oehlschlaeger MA. A shock tube study of methyl decanoate auto-ignition at elevated pressures. Combust Flame 2012;159:476–81.

[262] Akih-Kumgeh B, Bergthorson JM. Experimental and modeling study of trends in the high-temperature ignition of methyl and ethyl esters. Energy Fuels 2011;25:4345–56.

[263] McEnally CS, Pfefferle LD. Sooting tendencies of oxygenated hydrocarbons in laboratory-scale flames. Environ Sci Technol 2011;45:2498–503.

[264] Feng Q, Jalali A, Fincham AM, Wang YL, Tsotsis TT, Egolfopoulos FN. Soot formation in flames of model biodiesel fuels. Combust Flame 2012;159: 1876–93.

[265] Kholghy M, Weingarten J, Thomson MJ. A study of the effects of ester moiety on soot formation in a laminar coflow diffusion flame of a surrogate for B100 biodiesel. Proc Combust Inst 2014. http://dx.doi.org/10.1016/j.proci.2014.07.019 (in press).

[266] Feng Q, Wang YL, Tsotsis TT, Egolfopoulos FN. Formation of nitrogen oxides in flames of model biodiesel fuels. Ind Chem Eng Res 2012;51:9719–32.

[267] Sarathy SM, Thomson MJ, Pitz WJ, Lu T. An experimental and kinetic modeling study of methyl decanoate combustion. Proc Combust Inst 2011;33:399–405.

[268] Zhang K, Togbé C, Dayma G, Dagaut P. Experimental and kinetic modeling study of *trans*-methyl-3-hexenoate oxidation in JSR and the role of C=C double bond. Combust Flame 2014;161:818–25.

[269] Hansen AC, Zhang Q, Lyne PWL. Ethanol–diesel fuel blends – a review. Bioresour Technol 2005;96:277–85.

[270] Giakoumis EG, Rakopoulos CD, Dimaratos AM, Rakopoulos DC. Exhaust emissions with ethanol or *n*-butanol diesel fuel blends during transient operation: a review. Renew Sustain Energy Rev 2013;17:170–90.

[271] Alam FE, Liu YC, Avedisian CT, Dryer FL, Farouk TI. *n*-Butanol droplet combustion: numerical modeling and reduced gravity experiments. Proc Combust Inst 2014. http://dx.doi.org/10.1016/j.proci.2014.06.043 (in press).

[272] Ghiassi H, Toth P, Lighty JS. Sooting behaviors of *n*-butanol and *n*-dodecane blends. Combust Flame 2014;161:671–9.

[273] Danilov AM. Fuel additives: evolution and use in 1996–2000. Chem Technol Fuels Oils 2001;37:444–55.

[274] Ribeiro NM, Pinto AC, Quintella CM, da Rocha GO, Teixeira LS, Guarieiro LL, et al. The role of additives for diesel and diesel blended (ethanol or biodiesel) fuels: a review. Energy Fuels 2007;21:2433–45.

[275] Akih-Kumgeh B, Bergthorson JM. Tailoring ethanol high temperature ignition by means of chemical additives and water content. SAE Int J Fuels Lubr 2010;3:598–609.

[276] Goldsborough SS, Johnson MV, Banyon C, Pitz WJ, McNenly MJ. Experimental and modeling study of fuel interactions with an alkyl nitrate cetane enhancer, 2-ethyl-hexyl nitrate. Proc Combust Inst 2014. http://dx.doi.org/10.1016/j.proci.2014.06.048 (in press).

[277] Solantausta Y, Nylund NO, Westerholm M, Koljonen T, Oasmaa A. Wood-pyrolysis oil as fuel in a diesel-power plant. Bioresour Technol 1993;46(1–2):177–88.

[278] Meier D, Scholl S, Klaubert H, Markgraf J. Practical results from Pytec's biomass-to-oil (BTO) process with ablative pyrolyser and diesel CHP plant [Online]. Available: ⟨http://www.pytecsite.de/pytec_eng/publikationen.htm⟩; 2007 [accessed 2014].

[279] Mueller CJ. The feasibility of using raw liquids from fast pyrolysis of woody biomass as fuels for compression-ignition engines: a literature review. SAE Int J Fuels Lubr 2013;6(1):251–62. http://dx.doi.org/10.4271/2013-01-1691.

[280] Shihadeh A, Hochgreb S. Diesel engine combustion of biomass pyrolysis oils. Energy Fuels 2000;14(2):260–74.

[281] Shaddix CR, Hardesty DR. Combustion properties of biomass flash pyrolysis: final project report. Albuquerque: Sandia National Laboratories; 1999.

[282] Bertoli C, D'Alessio J, Del Giacomo N, Lazzaro M, Massoli P, Moccia V. Running light-duty DI diesel engines with wood pyrolysis oil. SAE Technical Paper No. 2000-01-2975; 2000.

[283] Van de Beld B, Holle E, Florijn J. The use of pyrolysis oil and pyrolysis oil derived fuels in diesel engines for CHP applications. Appl Energy 2013;102: 190–7.

[284] Ormrod Diesels Limited. Development of an internal combustion engine for use with crude pyrolysis oil. Department of Trade & Industry; 2000.

[285] Leech J. Running a dual fuel diesel engine on crude pyrolysis oil. Biomass gasification and pyrolysis, state of the art and future prospects. Newbury (UK): Editors: Kaltschmitt, M.; Bridgwater, A.V., CPL Press; 1997; 495–7.

[286] Bertoli C, Calabria R, D'Alessio J, Del Giacomo N, Lazzaro M, Massoli P, et al. Diesel engines fueled by wood pyrolysis oil: feasibility and perspectives. SAE Technical Paper No. 2001-24-0041; 2001.

[287] Lee S, Kim T, Kang K. Performance and emission characteristics of a diesel engine operated with wood pyrolysis oil. Inst Mech Eng Part D: J Automob Eng 2014;228(2):180–9. http://dx.doi.org/10.1177/0954407013502951.

[288] Chiaramonti D, Bonini M, Fratini E, Tondi G, Gartner K, Bridgwater AV, et al. Development of emulsions from biomass pyrolysis liquids and diesel and their use in engines – Part 1: emulsion production. Biomass Bioenergy 2002;25(1):85–99.

[289] Chiaramonti D, Bonini M, Fratini E, Tondi G, Gartner K, Bridgwater AV, et al. Development of emulsions from biomass pyrolysis liquid and diesel and their use in engines – Part 2: tests in diesel engines. Biomass Bioenergy 2002;25 (1):101–11.

[290] Lee S, Jang Y, Kim TY, Kang KY, Kim H, Lim J. Performance and emission characteristics of a diesel engine fueled with pyrolysis oil-ethanol blend with diesel and biodiesel pilot injection. SAE Int Fuels Lubr 2013; 6(3):785–93. http://dx.doi.org/10.4271/2013-01-2671.

[291] Mueller ME, Pitsch H. Large eddy simulation of soot evolution in an aircraft combustor. Phys Fluids 2013;25(11):110812.

[292] Lefebvre AH. Gas turbine combustion. Philadelphia (USA): CRC Press; 1998.

[293] Shanbhogue SJ, Husain S, Lieuwen T. Lean blowoff of bluff body stabilized flames: scaling and dynamics. Prog Energy Combust Sci 2009;35(1):98–120.

[294] Correa SM. Power generation and aeropropulsion gas turbines: from combustion science to combustion technology. Proc Combust Inst 1998;27: 1793–807.

[295] Richards GA, McMillian MM, Gemmen RS, Rogers WA, Cully SR. Issues for low-emission, fuel-flexible power systems. Prog Energy Combust Sci 2001;27:141–69.

[296] Stickles R, Barrett J. Continuous lower energy, emissions and noise (CLEEN) technologies development: TAPS II Technology. Final report – technology assessment, No. DOT/FAA/AEE/2014-03. FAA Contract DTFAWA-10-C-00046. ⟨http://www.faa.gov/about/office_org/headquarters_offices/apl/research/aircraft_technology/cleen/reports/media/TAPS_II_Public_Final_Report.pdf⟩; 2014 [accessed 21.09.14].

[297] Maurice LQ, Lander H, Edwards T, Harrison III WE. Advanced aviation fuels: a look ahead via a historical perspective. Fuel 2001;80(5):747–56.

[298] Colket M, Edwards T, Williams S, Cernansky NP, Miller DL, Egolfopoulos F, et al. Development of an experimental database and kinetic models for surrogate jet fuels. In: Proceedings of the 45th AIAA aerospace sciences meeting and exhibit. AIAA paper 2007-770; 2007. p. 8–11, http://dx.doi.org/10.2514/6.2007-770.

[299] Humer S, Frassoldati A, Granata S, Faravelli T, Ranzi E, Seiser R, et al. Experimental and kinetic modeling study of combustion of JP-8, its

surrogates and reference components in laminar non-premixed flows. Proc Combust Inst 2007;31:393–400.

[300] Dagaut P, Cathonnet M. The ignition, oxidation, and combustion of kerosene: a review of experimental and kinetic modeling. Prog Energy Combust Sci 2006;32:48–92.

[301] Dooley S, Won SH, Chaos M, Heyne J, Ju YG, Dryer FL, et al. A jet fuel surrogate formulated by real fuel properties. Combust Flame 2010;157: 2333–9.

[302] Dryer FL, Jahangirian S, Dooley S, Won SH, Heyne JS, Iyer VR, et al. Emulating the combustion behavior of real jet aviation fuels by surrogate mixtures of hydrocarbon fluid blends: implications for science and engineering. Energy Fuels 2014;28:3474–85.

[303] Violi A, Yan S, Eddings EG, Sarofim AF, Granata S, Faravelli T, et al. Experimental formulation and kinetic model for JP-8 surrogate mixtures. Combust Sci Technol 2002;174:399–417.

[304] Wang H, Dames E, Sirjean B, Sheen DA, Tangko R, Violi A, et al. A high-temperature chemical kinetic model of n-alkane (up to n-dodecane), cyclohexane, and methyl-, ethyl-, n-propyl and n-butyl-cyclohexane oxidation at high temperatures. JetSurF version 2.0. ⟨http://ignis.usc.edu/Mechanisms/Model%20release.html⟩; 2010.

[305] Blanquart G, Pepiot-Desjardins P, Pitsch H. Chemical mechanism for high temperature combustion of engine relevant fuels with emphasis on soot precursors. Combust Flame 2009;156:588–607.

[306] Dooley S, Dryer FL, Farouk TI, Ju Y, Won SH. Reduced kinetic models for the combustion of jet propulsion fuels. In: Proceedings of the 51st AIAA Aerospace Sciences Meeting, Dallas, TX. Paper 2013-0158; 2013, http://dx.doi.org/10.2514/6.2013-158.

[307] Munzar JD, Denman BM, Jimenez R, Zia A, Bergthorson JM. Flame speed and vapour pressure of biojet fuel blends. In: Proceedings of the ASME Turbo Expo 2013, ASME paper GT2013-94650; 2013.

[308] Allen C, Valco D, Toulson E, Edwards T, Lee T. Ignition behavior and surrogate modeling of JP-8 and of camelina and tallow hydrotreated renewable jet fuels at low temperatures. Combust Flame 2013;160:232–9.

[309] Wilson III GR, Edwards T, Corporan E, Freerks RL. Certification of alternative aviation fuels and blend components. Energy Fuels 2013;27:962–6.

[310] Hileman JI, Stratton RW, Donohoo PE. Energy content and alternative jet fuel viability. J Propuls Power 2010;26:1184–95.

[311] Carlson TR, Tompsett GA, Conner WC, Huber GW. Aromatic production from catalytic fast pyrolysis of biomass-derived feedstocks. Top Catal 2009;52(3): 241–252.

[312] Saffaripour M, Zabeti P, Kholghy M, Thomson MJ. An experimental comparison of the sooting behavior of synthetic jet fuels. Energy Fuels 2011;25:5584–93.

[313] Saffaripour M, Veshkini A, Kholghy M, Thomson MJ. Experimental investigation and detailed modeling of soot aggregate formation and size distribution in laminar coflow diffusion flames of Jet A-1, a synthetic kerosene, and n-decane. Combust Flame 2014;161:848–63.

[314] Dooley S, Won SH, Jahangirian S, Ju YG, Dryer FL, Wang HW, et al. The combustion kinetics of a synthetic paraffinic jet aviation fuel and a fundamentally formulated, experimentally validated surrogate fuel. Combust Flame 2012;159:3014–20.

[315] Munzar JD, Zia A, Versailles P, Jiménez R, Bergthorson JM, Akih-Kumgeh B. Comparison of laminar flame speeds, extinction stretch rates and vapor pressures of Jet A-1/HRJ biojet fuel blends. In: Proceedings of the ASME Turbo Expo 2014, Paper GT2014-2595; 2014. http://dx.doi.org/10.1115/GT2013-94650.

[316] Li B, Liu N, Zhao R, Zhang H, Egolfopoulos FN. Flame propagation of mixtures of air with high molecular weight neat hydrocarbons and practical jet and diesel fuels. Proc Combust Inst 2013;34:727–33.

[317] Ji C, Wang YL, Egolfopoulos FN. Flame studies of conventional and alternative jet fuels. J Propuls Power 2011;27(4):856–63. http://dx.doi.org/10.2514/1.B34105.

[318] Holley AT, You XQ, Dames E, Wang H, Egolfopoulos FN. Sensitivity of propagation and extinction of large hydrocarbon flames to fuel diffusion. Proc Combust Inst 2009;32:1157–63.

[319] Li B, Liu N, Zhao R, Egolfopoulos FN, Zhang H. Extinction studies of flames of heavy neat hydrocarbons and practical fuels. J Propuls Power 2013;29:352–61.

[320] Hui X, Kumar K, Sung CJ, Edwards T, Gardner D. Experimental studies on the combustion characteristics of alternative jet fuels. Fuel 2012;98:176–82.

[321] Hui X, Sung CJ. Laminar flame speeds of transportation-relevant hydrocarbons and jet fuels at elevated temperatures and pressures. Fuel 2013;109:191–200.

[322] Kick T, Herbst J, Kathrotia T, Marquetand J, Braun-Unkhoff M, Naumann C, et al. An experimental and modeling study of burning velocities of possible future synthetic jet fuels. Energy 2012;43:111–23.

[323] Won S, Veloo PS, Santner J, Ju Y, Dryer FL. Comparative evaluation of global combustion properties of alternative jet fuels. In: Proceedings of the 51st AIAA aerospace sciences meeting, Dallas. TX. Paper 2013-0156; 2013, http://dx.doi.org/10.2514/6.2013-156.

[324] Rye L, Wilson C. The influence of alternative fuel composition on gas turbine ignition performance. Fuel 2012;96:277–83.

[325] Mastorakos E. Ignition of turbulent non-premixed flames. Prog Energy Combust Sci 2009;35(1):57–97.

[326] Won SH, Sun W, Ju Y. Kinetic effects of toluene blending on the extinction limit of n-decane diffusion flames. Combust Flame 2010;157:411–20.

[327] Won SH, Dooley S, Dryer FL, Ju Y. A radical index for the determination of the chemical kinetic contribution to diffusion flame extinction of large hydrocarbon fuels. Combust Flame 2012;159:541–51.

[328] Wang W, Oehlschlaeger MA. Auto-ignition studies of conventional and Fischer–Tropsch jet fuels. Fuel 2012;98:249–58.

[329] Valco D, Gentz G, Allen C, Colket M, Edwards T, Gowdagiri S, et al. Auto-ignition behavior of synthetic alternative jet fuels: an examination of chemical composition effects on ignition delays at low to intermediate temperatures. Proc Combust Inst 2014. http://dx.doi.org/10.1016/j.proci.2014.05.145 (in press).

[330] Zhu Y, Li S, Davidson DF, Hanson RK. Ignition delay times of conventional and alternative fuels behind reflected shock waves. Proc Combust Inst 2014. http://dx.doi.org/10.1016/j.proci.2014.05.034 (in press).

[331] Shen HPS, Steinberg J, Vanderover J, Oehlschlaeger MA. A shock tube study of the ignition of n-heptane, n-decane, n-dodecane, and n-tetradecane at elevated pressures. Energy Fuels 2009;23:2482–9.

[332] Wey D, Bulzan D. Effects of bio-derived fuels on emissions and performance using a 9-point lean direct injection low emissions concept. In: Proceedings of the ASME Turbo Expo 2013, ASME paper GT2013-94888; 2013.

[333] Bradley TH, Frank AA. Design, demonstrations and sustainability impact assessments for plug-in hybrid electric vehicles. Renew Sustain Energy Rev 2009;13:115–28.

[334] Wunning JA, Wunning JG. Flameless oxidation to reduce thermal NO-formation. Prog Energy Combust Sci 1997;23:81–94.

[335] Cavaliere A, de Joannon M. Mild combustion. Prog Energy Combust Sci 2004;30:329–66.

[336] Lu X, Han D, Huang Z. Fuel design and management for the control of advanced compression–ignition combustion modes. Prog Energy Combust Sci 2011;37:741–83.

[337] Dec JE, Hwang W, Sjöberg M. An investigation of thermal stratification in HCCI engines using chemi-luminescence imaging (No. 2006-01-1518). SAE Technical Paper; 2006, http://dx.doi.org/10.4271/2006-01-1518.

[338] He BQ, Yuan J, Liu MB, Zhao H. Combustion and emission characteristics of a n-butanol HCCI engine. Fuel 2014;115:758–64.

[339] He BQ, Liu MB, Yuan J, Zhao H. Combustion and emission characteristics of a HCCI engine fuelled with n-butanol–gasoline blends. Fuel 2013;108:668–74.

[340] Baumgardner ME, Sarathy SM, Marchese AJ. Auto-ignition characterization of primary reference fuels and n-heptane/n-butanol mixtures in a constant volume combustion device and homogeneous charge compression ignition engine. Energy Fuels 2013;27(12):7778–89.

[341] Kokjohn SL, Hanson RM, Splitter DA, Reitz RD. Fuel reactivity controlled compression ignition (RCCI): a pathway to controlled high-efficiency clean combustion. Int J Engine Res 2011;12:209–26.

[342] Vuilleumier D, Kozarac D, Mehl M, Saxena S, Pitz WJ, Dibble RW, et al. Intermediate temperature heat release in an HCCI engine fueled by ethanol/n-heptane mixtures: an experimental and modeling study. Combust Flame 2014;161:680–95.

[343] Naidja A, Krishna CR, Butcher T, Mahajan D. Cool flame partial oxidation and its role in combustion and reforming of fuels for fuel cell systems. Prog Energy Combust Sci 2003;29:155–91.

[344] Starikovskaia SM. Plasma assisted ignition and combustion. J Phys D: Appl Phys 2006;39(16):R265.

[345] Starikovskiy A, Aleksandrov N. Plasma-assisted ignition and combustion. Prog Energy Combust Sci 2013;39:61–110.

[346] Starikovskaia SM. Plasma-assisted ignition and combustion: nanosecond discharges and development of kinetic mechanisms. J Phys D: Appl Phys 2014;47(35):353001.

[347] Ju Y. Recent progress and challenges in fundamental combustion research. Adv Mech 2014;44:201402. http://dx.doi.org/10.6052/1000-0992-14-011.

[348] Sun W, Ju Y. Nonequilibrium plasma-assisted combustion: a review of recent progress. J Plasma Fusion Res 2013;89:208–19.

[349] Cathey CD, Tang T, Shiraishi T, Urushihara T, Kuthi A, Gundersen MA. Nanosecond plasma ignition for improved performance of an internal combustion engine. IEEE Trans Plasma Sci 2007;35(6):1664–8.

[350] Shiraishi T, Urushihara T, Gundersen M. A trial of ignition innovation of gasoline engine by nanosecond pulsed low temperature plasma ignition. J Phys D: Appl Phys 2009;42(13):135208.

[351] Tropina AA, Lenarduzzi L, Marasov SV, Kuzmenko AP. Comparative analysis of engine ignition systems. IEEE Trans Plasma Sci 2009;37(12):2286–92.

[352] Lefkowitz JK, Ju Y, Tsuruoka R, Ikeda Y. A study of plasma-assisted ignition in a small internal combustion engine. AIAA paper-2012-1133; 2012. http://dx.doi.org/10.2514/6.2012-1133.

[353] Mueller CJ, Upatnieks A. Dilute clean diesel combustion achieves low emissions and high efficiency while avoiding control problems of HCCI. In: Proceedings of the 11th Annual diesel engine emissions reduction (DEER) conference; 2005. http://energy.gov/sites/prod/files/2014/03/f9/2005_deer_mueller.pdf.

[354] Singh S, Reitz RD, Musculus MPB, Lachaux T. Validation of engine combustion models against detailed in-cylinder optical diagnostics data for a heavy-duty compression-ignition engine. Int J Engine Res 2007;8(1):97–126.

[355] Kalghatgi GT. The outlook for fuels for internal combustion engines. Int J Engine Res 2014;15(4):383–98. http://dx.doi.org/10.1177/1468087414526189.

[356] Nightingale NP.. Automotive Stirling engine. MOD II Design Report. Stirling Engine Systems Division, MTI, Latham NY, NASA Report CR-175106. ⟨http://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19880002196.pdf⟩; 1986.

[357] Richey AE. Mod II automotive Stirling engine design description and performance projections. SAE Technical Paper No. 860059; 1986, http://dx.doi.org/10.4271/860059.

[358] Farrell RA. Mod II Stirling engine overview. SAE Technical Paper No. 880539; 1988, http://dx.doi.org/10.4271/880539.

[359] Heywood JB. Automotive engines and fuels: a review of future options. Prog Energy Combust Sci 1981;7(3):155–84.

[360] Evans RL. Automotive engine alternatives. Springer US; 1987. ISBN:978-1-4757-9350-5 (Print) 978-1-4757-9348-2 (Online), http://dx.doi.org/10.1007/978-1-4757-9348-2.

[361] Gomez A, Berry JJ, Roychoudhury S, Coriton B, Huth J. From jet fuel to electric power using a mesoscale, efficient Stirling cycle. Proc Combust Inst 2007;31:3251–9.

[362] Weinberg FJ. Heat-recirculating burners: principles and some recent developments. Combust Sci Technol 1996;121(1–6):3–22.

[363] Lloyd SA, Weinberg FJ. Limits to energy release and utilization from chemical fuels. Nature 1975;257:367–70.

[364] Wood S, Harris AT. Porous burners for lean-burn applications. Prog Energy Combust Sci 2008;34:667–84.

[365] Mujeebu MA, Abdullah MZ, Abu Bakar MZ, Mohamad AA, Abdullah MK. A review of investigations on liquid fuel combustion in porous inert media. Prog Energy Combust Sci 2009;35:216–30.

[366] Hardesty DR, Weinberg FJ. Burners producing large excess enthalpies. Combust Sci Technol 1973;8:201–14.

[367] Weinberg FJ, Rowe DM, Min G, Ronney PD. On thermoelectric power conversion from heat recirculating combustion systems. Proc Combust Inst 2002;29(1):941–7.

[368] Cho JH, Lin CS, Richards CD, Richards RF, Ahn J, Ronney PD. Demonstration of an external combustion micro-heat engine. Proc Combust Inst 2009;32(2):3099–105.

[369] Echekki T, Haroldsen BL, Krafcik KL, Morales AM, Mills BE, Liu S, et al. Design and fabrication of a meso-scale Stirling engine and combustor. Sandia National Laboratories Report No. SAND2005-2340; 2005, http://dx.doi.org/10.2172/876337.

[370] Gauthier GP, Watson GMG, Bergthorson JM. Burning rates and temperatures of flames in heat-recirculating burners: a numerical study of flame propagation in small heat-recirculating tubes. Combust Flame 2014;161:2348–60.

[371] Stirling engine image, Stirling_Animation.gif. ⟨http://en.wikipedia.org/wiki/Stirling_engine#mediaviewer/File:Stirling_Animation.gif⟩ [accessed 26.09.14].

[372] Lloyd SA, Weinberg FJ. Burner for mixtures of very low heat content. Nature 1974;251:47–9.

[373] Howell JR, Hall MJ, Ellzey JL. Combustion of hydrocarbon fuels within porous inert media. Prog Energy Combust Sci 1996;22:121–45.

[374] Ju Y, Maruta K. Microscale combustion: technology development and fundamental research. Prog Energy Combust Sci 2011;37:669–715.

[375] Schoegl I, Ellzey JL. Superadiabatic combustion in conducting tubes and heat exchangers of finite length. Combust Flame 2007;151:142–59.

[376] Farra N, Tzanetakis T, Thomson MJ. Experimental determination of the efficiency and emissions of a residential microcogeneration system based on a Stirling engine and fueled by diesel and ethanol. Energy Fuels 2012;26:889–900.

[377] Joensen F, Rostrup-Nielsen JR. Conversion of hydrocarbons and alcohols for fuel cells. J Power Sources 2002;105:195–201.

[378] Deluga GA, Salge JR, Schmidt LD, Verykios XE. Renewable hydrogen from ethanol by autothermal reforming. Science 2004;303:993–7.

[379] Pettersson LJ, Westerholm R. State of the art of multi-fuel reformers for fuel cell vehicles: problem identification and research needs. Int J Hydrog Energy 2001;26:243–64.

[380] Smith CH, Pineda DI, Zak CD, Ellzey JL. Conversion of jet fuel and butanol to syngas by filtration combustion. Int J Hydrog Energy 2013;38:879–89.

[381] Dixon MJ, Schoegl I, Hull CB, Ellzey JL. Experimental and numerical conversion of liquid heptane to syngas through combustion in porous media. Combust Flame 2008;154:217–31.

[382] Chaubey R, Sahu S, James OO, Maity S. A review on development of industrial processes and emerging techniques for production of hydrogen from renewable and sustainable sources. Renew Sustain Energy Rev 2013;23:443–62.

[383] Sobacchi MG, Saveliev AV, Fridman AA, Kennedy LA, Ahmed S, Krause T. Experimental assessment of a combined plasma/catalytic system for hydrogen production via partial oxidation of hydrocarbon fuels. Int J Hydrog Energy 2002;27:635–42.

[384] Tao X, Bai M, Li X, Long H, Shang S, Yin Y, et al. CH_4–CO_2 reforming by plasma – challenges and opportunities. Prog Energy Combust Sci 2011;37(2):113–24.

[385] Mongia HC. TAPS: a fourth generation propulsion combustor technology for low emissions. AIAA paper 2003-2657; 2003, http://dx.doi.org/10.2514/6.2003-2657.

[386] Mongia HC. On continuous NO_x reduction of aero-propulsion engines. AIAA paper 2010-1329; 2010, http://dx.doi.org/10.2514/6.2010-1329.

[387] Foust MJ, Thomsen D, Stickles R, Cooper C, Dodds W. Development of the GE aviation low emissions TAPS combustor for next generation aircraft engines. AIAA Paper 2012-936; 2012, http://dx.doi.org/10.2514/6.2012-936.

[388] Won SH, Windom B, Jiang B, Ju Y. The role of low temperature fuel chemistry on turbulent flame propagation. Combust Flame 2014;161(2):475–83.

[389] Oran ES, Gardner JH. Chemica–acoustic interactions in combustion systems. Prog Energy Combust Sci 1985;11:253–76.

[390] Lieuwen T. Modeling premixed combustion–acoustic wave interactions: a review. J Propuls Power 2003;19(5):765–81.

[391] Konle M, Kiesewetter F, Sattelmayer T. Simultaneous high repetition rate PIV–LIF-measurements of CIVB driven flashback. Exp Fluids 2008;44(4):529–38.

[392] Eichler C, Sattelmayer T. Premixed flame flashback in wall boundary layers studied by long-distance micro-PIV. Exp Fluids 2012;52(2):347–60.

[393] Fritz J, Kroner M, Sattelmayer T. Flashback in a swirl burner with cylindrical premixing zone. J Eng Gas Turbines Power 2004;126(2):276–83.

[394] McManus KR, Poinsot T, Candel SM. A review of active control of combustion instabilities. Prog Energy Combust Sci 1993;19(1):1–29.

[395] Pilla G, Galley D, Lacoste DA, Lacas F, Veynante D, Laux CO. Stabilization of a turbulent premixed flame using a nanosecond repetitively pulsed plasma. IEEE Trans Plasma Sci 2006;34(6):2471–7.

[396] Herbon JT, Bennett GA, Dean AJ, Idelchik MS, Saddoughi SG, Younsi A. Premixed, preswirled plasma-assisted pilot. U.S. Patent Application 12/005,807. Publication Number US 2009/0165436 A1; 2007.

[397] Serbin S, Mostipanenko A, Matveev I, Tropina A. Improvement of the gas turbine plasma assisted combustor characteristics. In: Proceedings of the 49th AIAA aerospace sciences meeting including the new horizons forum and aerospace exposition; 2011. AIAA paper 2011-61, http://dx.doi.org/10.2514/6.2011-61.

[398] Lacoste DA, Xu DA, Moeck JP, Laux CO. Dynamic response of a weakly turbulent lean-premixed flame to nanosecond repetitively pulsed discharges. Proc Combust Inst 2013;34(2):3259–66.

[399] Lacoste DA, Moeck JP, Paschereit CO, Laux CO. Effect of plasma discharges on nitric oxide emissions in a premixed flame. J Propuls Power 2013;29(3):748–51.

[400] Evans MDG, Versailles P, Sainct FP, Bergthorson JM, Coulombe S. Increased flame reactivity of a lean premixed flame through the use of a custom-built high-voltage pulsed Plasma Source. IEEE Trans Plasma Sci 2014;42(10):2844–2845. http://dx.doi.org/10.1109/TPS.2014.2330552 (in press).

[401] Moeck JP, Lacoste DA, Laux CO, Paschereit CO. Control of combustion dynamics in a swirl-stabilized combustor with nanosecond repetitively pulsed discharges. AIAA paper-2013-565; 2013, http://dx.doi.org/10.2514/6.2013-565.